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Report RMD 5043-Q3-64

Contract No. NOnr 4364(00)

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## ADVANCED OXIDIZER RESEARCH

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Report Period: 1 July 1964 to 30 September 1964

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#### GENERAL FOREWORD

This quarterly report was prepared by the Thiokol Chemical Corporation, Reaction Motors Division, Denville, New Jersey, and summarizes work in the area of advanced oxidizer chemistry being conducted at this Division under the sponsorship of the Advanced Research Projects Agency. The work was administered by the Department of the Navy, Office of Naval Research, with Mr. R. L. Hanson serving as Scientific Officer, and includes the following tasks:

Section	Task No.	Title
I	51	Difluoramine Chemistry
II	52	Synthesis of Compounds for Structure-Sensitivity Study
III	53	Chemistry of the Oxygen Subfluorides
IV	55	Thermal Stability of Advanced Solid Oxidizers
V	56 & 54	Chemistry of Difluorodiazine and Nitrosyl Fluoride and Stabilization of Nitronium Perchlorate

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## ABSTRACT

This report describes research conducted at Thiokol Chemical Corporation Reaction Motors Division directed toward the development of advanced solid oxidizers. The five major tasks on which work has been performed are listed below, together with an abstract of each task, and are included as five separate sections of this report. Work on Task 54 was terminated during this quarter and the data obtained for this task have been combined with the data of Task 56.

### SECTION I - DIFLUORAMINE CHEMISTRY

A 4.5 gm sample of 1, 1-bis (difluoramino) heptane ~~has been~~ prepared and submitted, ~~along with evidence of its purity,~~ to the Bureau of Mine Laboratories for thermochemical studies. The dehydrofluorination of the gem-compound at 40°C led to the loss of two equivalents of hydrogen fluoride, even though only one equivalent of the basic ion-exchange resin was used

Ethyl-N-cyclohexylcarbamate, an intermediate in the synthesis of cyclohexylidenefluorimine, was obtained from the reaction of cyclohexylamine and ethyl chloroformate in 95.5% yield. Fluorination of the carbamate in aqueous suspension appeared to proceed as expected; work-up of the product has not yet been completed.

Photolysis of 1,4-bis(fluoramino)cyclohexane-2 yielded only degradation products and insoluble polymeric material. Treatment of the bis(fluorimine) with boron trifluoride did not result in tautomerization to an aromatic structure.

The synthesis of t-butyldifluoramine has been repeated to obtain an analytically pure sample of the material.

### SECTION II - SYNTHESIS OF COMPOUNDS FOR STRUCTURE-SENSITIVITY STUDY

Work is reported on the synthesis and gas chromatographic purification of aliphatic difluoramines for evaluation of the relationship between structure and sensitivity. An investigation was made of the chromatographic conditions aimed at obtaining adducts that are > 99% pure. In addition, 18 gm of chromatographically pure 1,1-bis(difluoramino)cyclohexane was synthesized and, after

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chromatographic purification, was submitted to the Naval Ordnance Laboratory for sensitivity measurements.

### SECTION III - CHEMISTRY OF THE OXYGEN SUBFLUORIDES

The reaction of  $O_2F_2$  with  $CsCl$  appears to produce an active fluorine containing solid with an approximate  $Cs:F:Cl$  ratio of 1:1:0.5. The solid also contains oxygen, but direct determination of its oxygen content has not been made.

Reactions of  $O_3F_2$  with  $Cl_2$ ,  $AsF_3$ , and  $NO$  failed to produce any products of interest.

The reaction of  $NF_2$  with  $O_2AsF_5$  yielded  $NF_3$  and  $O_2$  in the gas phase and an unidentified solid with an x-ray pattern which differs from that of  $O_2AsF_5$ .

On the basis of an assumption that the lattice energy of  $O_2^+ClO_4^-$  should be the same as that of  $NO^+ClO_4^-$ , a heat of formation of +6.4 kcal/mole was calculated for  $O_2^+ClO_4^-$ .

### SECTION IV - THERMAL STABILITY OF ADVANCED SOLID OXIDIZERS

The thermal decomposition of hydrazinium perchlorate has been studied in the range  $140^\circ C$  to  $200^\circ C$ . A plot of the slope of the linear portion of the decomposition curve versus reciprocal absolute temperature gives an  $E_a$  of 23.8 kcal/mole throughout this range.

Experimental evidence tends to confirm the proposed stoichiometry,  $8 N_2H_5ClO_4 \longrightarrow 7 NH_4ClO_4 + NH_4Cl + 4 N_2 + 4 H_2O$ , based on decompositions of hydrazine and its salts previously reported in the literature. The presence of  $NH_4^+$ ,  $Cl^-$ , and  $N_2$  as products has been definitely established.

Crude samples of hydroxylammonium perchlorate have been prepared and are being further purified.

### SECTION V - CHEMISTRY OF DIFLUORODIAZINE AND NITROSYL FLUORIDE AND STABILIZATION OF NITRONIUM PERCHLORATE

The reactions of  $N_2FAsF_5$  with  $AgClO_4$  and with  $NH_4SO_2F$  in HF at room temperature yield equimolar  $N_2O \cdot ClO_4F$  and  $N_2O \cdot SO_2F$  mixtures, respectively.

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Report RMD 5043 Q3-64

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Some evidence for the occurrence of desired ion-exhange reactions was obtained when  $N_2FAsF_6$ -HF solutions were treated with  $CsClF_4$  and with  $CsBrF_4$ .

$cis$ - $N_2F_2$  failed to form complexes with  $BiF_5$ ,  $PF_5$ ,  $SF_4$ ,  $SO_3$ ,  $ClF_3$ ,  $BrF_3$ , and  $BrF_5$ .

The addition of  $cis$ - $N_2F_2$  to liquid  $NOF \cdot 3HF$  complex appears, on the basis of NMR observations, to destroy the complex.

Attempts to isolate perchloric acid complexes of  $NO_2ClO_4$  or  $HONH_3ClO_4$  were unsuccessful.

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Report RMD 5043-Q3-64

**Section I**

**Task 51**

**DIFLUORAMINE CHEMISTRY**

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**Section I**

**DIFLUORAMINE CHEMISTRY**

**Harry F. Smith**

**Report RMD 5043-Q3-64**

**RMD Project 5043, Task 51**  
**Report Period: 1 July 1964 to**  
**30 September 1964**

**Contract No. NOnr 4364(00)**  
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**Project Code 4910**

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**FOREWORD**

This section of the quarterly progress report on advanced oxidizers describes research conducted from 1 July 1964 to 30 September 1964 on the synthesis and chemical reactions of organic fluoronitrogen compounds.

Technical personnel contributing to this effort were: H. F. Smith (Project Scientist), J. A. Castellano (Synthesis), J. Creatura and A. Fremmer (Chemical Analysis), and R. Storey, D. Kates, and R. Crooker (Instrumental Analysis).

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Task 51  
Report RMD 5043-Q3-64

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**CONTENTS**

	<b>Page</b>
I. INTRODUCTION	1
II. DISCUSSION	2
A. Synthesis and Purification of 1,1-Bis (difluoramino)heptane	2
B. Dehydrofluorination of 1,1-Bis (difluoramino)heptane	6
C. Synthesis of Cyclohexylidenefluorimine	6
D. Reactions of 1,4-Bis (fluorimino)cyclohexene-2	8
E. Synthesis and Purification of <u>t</u> -Butyldifluoramine	10
III. EXPERIMENTAL	12
A. 1,1-Bis (difluoramino)heptane	12
B. Ethyl-N-Cyclohexylcarbamate	12
C. Cyclohexyldifluoramine	13
D. <u>t</u> -Butyldifluoramine	13
IV. FUTURE WORK	14
V. REFERENCES	15

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## ILLUSTRATIONS

Figure		Page
1	Infrared Absorption Spectrum of 1,1-Bis(difluoramino)-heptane	4
2	Gas-Liquid Chromatogram of 1,1-Bis(difluoramino)-heptane	5
3	Changes in Ultraviolet Absorption Spectrum of 1,4-Bis(fluorimino)cyclohexene-2 During Photolysis	9

## TABLES

Table		Page
I	Reaction of <u>n</u> -Heptanal with Difluoramine	2
II	Conditions for GLC of 1,1-Bis(difluoramino)heptane	3

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## I. INTRODUCTION

The objective of this research program is the investigation of the chemical reactions of difluoraminoalkanes and related organic fluoronitrogen compounds. Information developed in the course of these studies is expected to be of value to the propellant field in several ways. An understanding of the fundamental chemistry of the difluoramino and fluorimino groups will be of aid both in the utilization of existing compounds in practical propellant formulations and in the search for new materials offering a more suitable balance between available energy and sensitivity. In addition, the exploration of the chemical reactivities of such compounds may provide a bonus in the form of prototype propellant ingredients of new structural types.

During the present report period the chemistry of the fluorimino group has continued to receive predominant emphasis as a consequence of the widespread interest in the addition reactions of this functionality in perfluoroguanidine. Our studies on the reactions of 1,2-bis(fluorimino)cyclohexane are now essentially complete and the program is being extended in two directions. Efforts to prepare 1-difluoramino-1-fluoriminoheptane and utilize it as a model compound more closely analogous to perfluoroguanidine are continuing. The synthesis of cyclohexylidenefluorimine has also been initiated; it will serve as a model of a simple fluorimine in reaction studies where bis(fluorimino)cyclohexane proved to be inappropriate.

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## II. DISCUSSION

## A SYNTHESIS AND PURIFICATION OF 1,1-BIS(DIFLUORAMINO)HEPTANE

Repetition of the reaction of heptanal with difluoramine (Ref 1) was necessary to provide a quantity of 1,1-bis(difluoramino)heptane (III) for further study of the dehydrofluorination reaction and eventually to supply sufficient amidine (VI) for research on its reactions. In addition, at the request of the Office of Naval Research, we undertook to provide a 5-gram sample of high-purity (III) for thermochemical studies at the Bureau of Mines Laboratories.

The results of three experiments are summarized in Table I. The reactions which occur in this preparation are shown in equation 1.

TABLE I  
REACTION OF n-HEPTANAL WITH DIFLUORAMINE

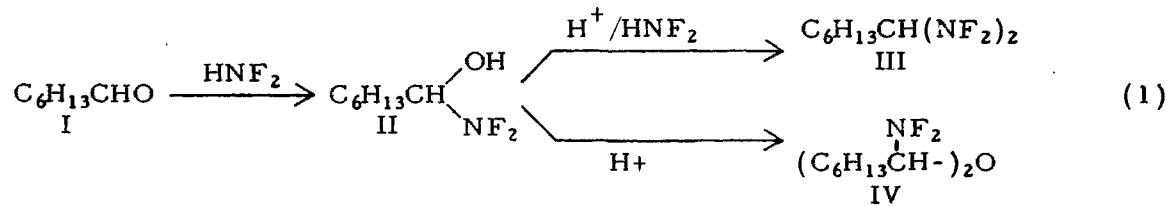
Experiment No.	Reflux Temp (°C)	gem-cpd (III) (gm)	gem-cpd (III) (%)	Ether (IV) (gm)	Ether (IV) (%)
1	-78	4.30	40.5	0.75	9.0
2	-25 <sup>a</sup>	1.00	9.5	1.00	12.0
3	-25 <sup>a</sup>	1.15	10.9	1.85	22.2

a Inadvertent use of  $CCl_2$  in the Dry ice condenser in place of a  $CHCl_3/CCl_4$  mixture gave the higher reflux temperature. The substantial loss of  $HNF_2$  permitted the formation of the ether at the expense of gem-bis(difluoramine).

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The three portions of III were combined and distilled to yield 5.35 gm of product which was  $97.0 \pm 0.5\%$  pure by weight, calculated from the results of elemental analysis with the assumption that the disparity was due to contamination by the starting aldehyde. Two additional distillations under reduced pressure (bp 61.5 to  $62.0^\circ\text{C}/15.1\text{ mmHg}$ ; 64.5 to  $65.0^\circ\text{C}/17.3\text{ mmHg}$ ) gave a product of purity  $\geq 98.5\%$ .

The assumption that n-heptanal constituted the principal contaminant is supported by both infrared and gas chromatographic data. The infrared absorption spectrum (Figure 1) is sharply defined and reveals a very small (ca 1%) carbonyl absorption band at  $1730\text{ cm}^{-1}$ . The gas-liquid chromatogram is reproduced in Figure 2. Although the baseline is slightly inconstant, the small shoulder preceding the major peak is probably significant. The retention time to this shoulder corresponds roughly to that of the aldehyde under the conditions employed (Table II).

TABLE II

CONDITIONS FOR GAS-LIQUID CHROMATOGRAM OF  
1, 1-BIS(DIFLUORAMINO)HEPTANE

Column:	Kel-F 200 on 60/80 Chromosorb P, 3 feet
Column Temp:	$85^\circ\text{C}$
Injector Temp:	$105^\circ\text{C}$
Detector Temp:	$260^\circ\text{C}$
Collector Temp:	$245^\circ\text{C}$
Flowrate:	28 ml/min
Sample:	2 $\mu\text{l}$
Attenuation:	X2

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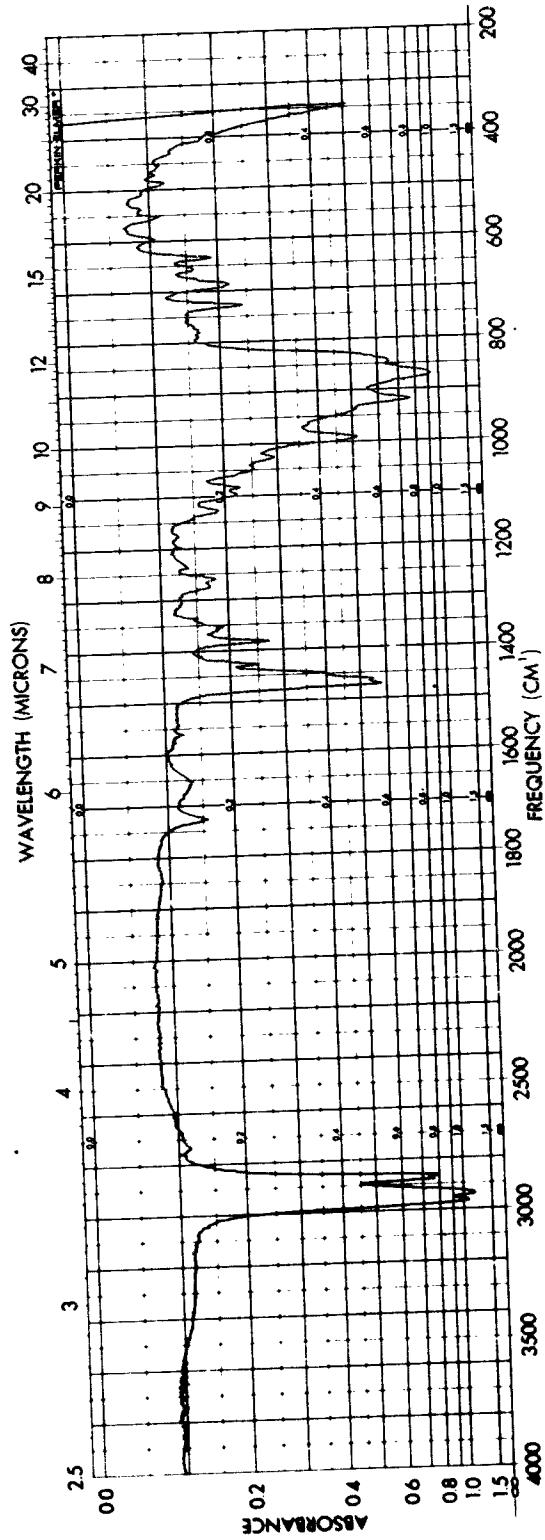


Figure 1. Infrared Absorption Spectrum of 1,1-Bis(difluoromino)heptane

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Task 51  
Report RMD 5043-Q3-64

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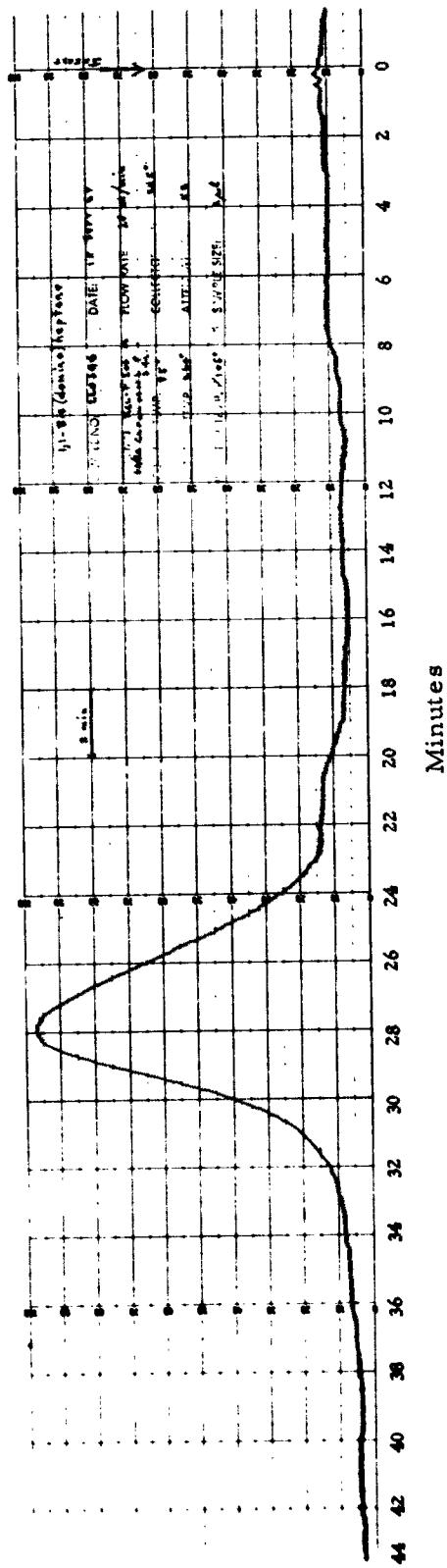


Figure 2. Gas-Liquid Chromatogram of 1,1-Bis(difluoromino)heptane

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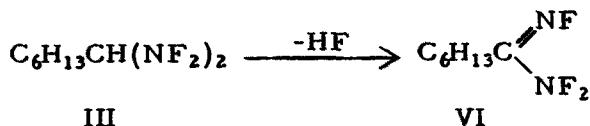
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### B. DEHYDROFLUORINATION OF 1,1-BIS(DIFLUORAMINO)HEPTANE

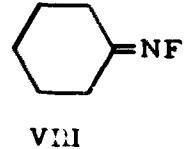
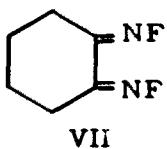
As reported earlier (Ref 1), the room temperature reaction of 1,1-bis(difluoramino)heptane with two equivalents of a weakly basic ion-exchange resin led to the formation of a product having the composition  $C_7H_{12}N_2F_2$  (V). In a subsequent small-scale experiment utilizing one equivalent of the resin at  $< 20^\circ C$ , a different product was obtained, but was consumed in analysis before its structure could be established.

During the current quarter an attempt was made to repeat the latter experiment on a slightly larger scale. Due to a mechanical failure, however, the reaction mixture was heated to  $40^\circ C$  for a short period. Under these conditions, even though only one equivalent of the base was present, the product obtained was identical to V. Further work will be required to determine the necessary conditions for the synthesis of the amidine and to characterize the product V.



### C. SYNTHESIS OF CYCLOHEXYLIDENEFLUORIMINE

Studies of the chemistry of the fluorimino group up to this point have utilized bis(fluorimino) compounds, principally 1,2-bis(fluorimino)cyclohexane (VII) as models. Although these investigations have produced a substantial amount of useful information (Ref 1 and 2), there remain some questions which can best be answered by experimentation on a simpler model, such as cyclohexylidenefluorimine (VIII). Either steric or electronic factors may operate to pre-



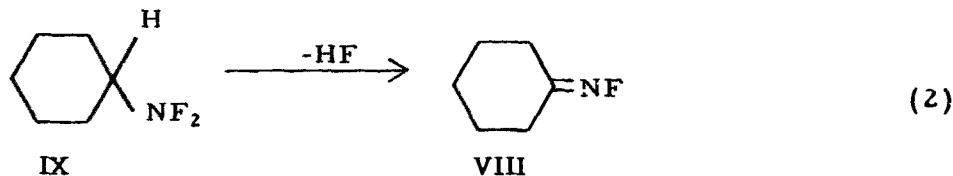
vent some of the expected reactions of the  $>C=NF$  grouping in VII. It is therefore desirable to reinvestigate some of the addition reactions which were unsuccessful with VII, using VIII.

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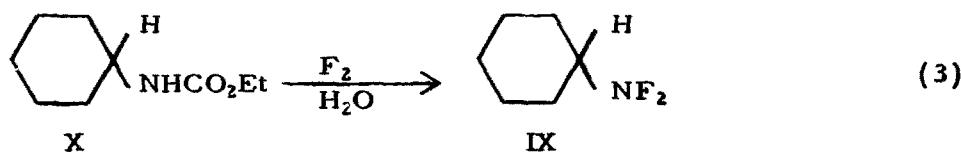
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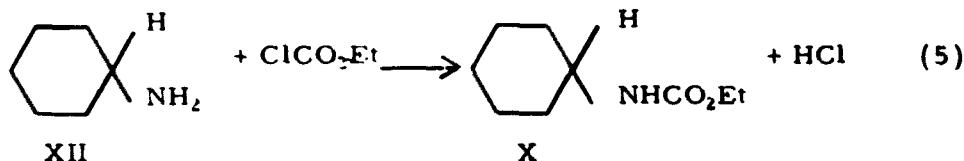
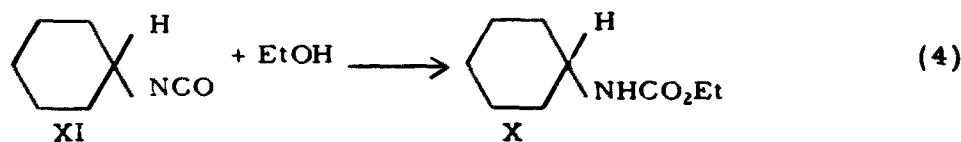
The obvious synthetic approach to VII involves the dehydrofluorination of difluoraminocyclohexane (IX).



The preparation of the required difluoramine by aqueous fluorination of ethyl-N-cyclohexylcarbamate has been described (Ref 3).



The carbamate, although no longer available commercially, is obtainable by either of two routes.



The method shown in equation 5, based on a published synthesis of the analogous benzyl compound (Ref 4), was chosen for this work and has proven to be highly successful. On a one-mole scale the reaction of cyclohexylamine with ethyl chloroformate in the presence of sodium hydroxide has yielded the carbamate

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in 95.5% yield, mp 52 to 54.5°C (Lit. mp 56°C, Ref 5; 56 to 58°C, Ref 6). This material was used in the next step of the synthesis sequence without further purification.

A suspension of ethyl-N-cyclohexylcarbamate in water was treated with nitrogen-diluted fluorine at <10°C. Although work-up of the reaction mixture has not yet been completed, there is evidence that the fluorination was at least partially successful. Coagulation of the suspended solid into a pasty mass indicated that at least some liquid products had been formed.

#### D. REACTIONS OF 1,4-BIS(FLUORIMINO)CYCLOHEXENE-2

##### 1. Photolysis

The stringent conditions of the first preparative scale photolysis of 1,4-bis(fluorimino)cyclohexene (Ref 1) have been moderated in an attempt to obtain useful intermediates or identifiable products. In the second experiment, the light source was filtered through Vycor (50% cutoff at 240 m $\mu$ ) and a greater depth of solution was exposed in order to obtain more efficient mixing during the exposure.

Under these conditions, the characteristic absorption peak of the bis(fluorimine) (XIII) at 238-240 m $\mu$  decreased regularly during the exposure (Figure 3). No other absorptions appeared in the ultraviolet or visible regions of the spectrum. The principal product was, as in the earlier experiment, an insoluble brown solid. This material, apparently polymeric, contained relatively few N-F linkages as indicated by infrared analysis. The cyclohexane solution contained a substantial quantity of unreacted starting material and a small amount of poorly defined degradation product. It can be concluded from these experiments that the direct photolysis of 1,4-bis(fluorimino)cyclohexane-2 is of no interest as a synthetic tool. The possibility that photo-initiated reactions with various reagents might be able to give useful products is, however, not precluded by these results.

##### 2. Attempted Aromatization

The tautomeric relationship that exists, at least in principle, between 1,4-bis(fluorimino)cyclohexene-2 (XIII) and the corresponding bis(fluoramino)benzene (XIV) has been noted previously (Ref 7). In a comparable case the diketone (XV)

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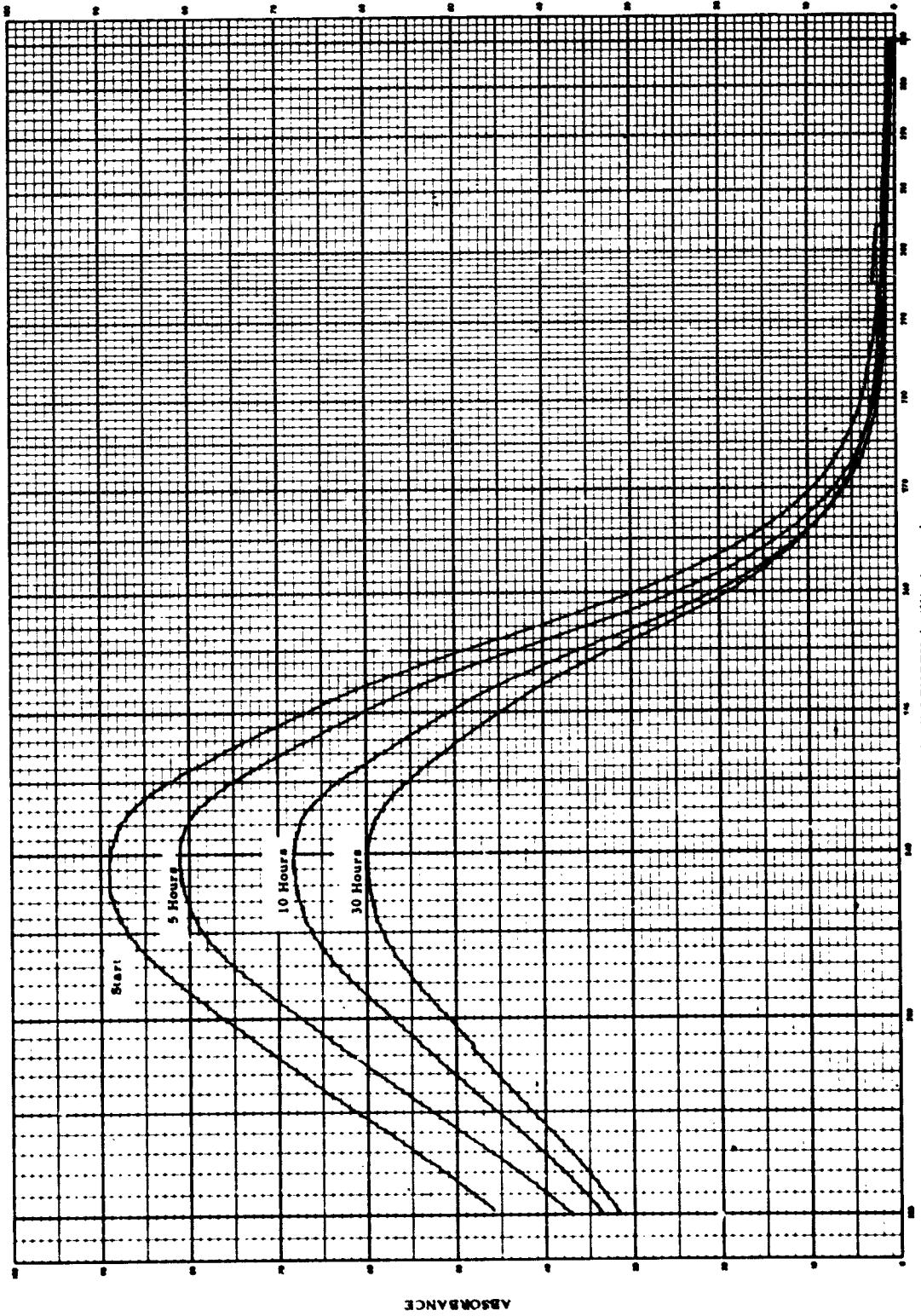
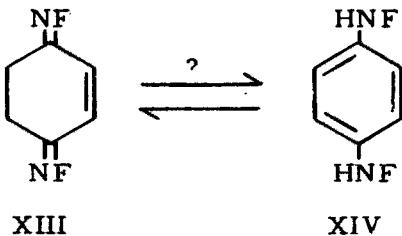


Figure 3. Changes in Ultraviolet Absorption Spectrum of 1,4-Bis(Fluorimino)cyclohexene-2 during Photolysis

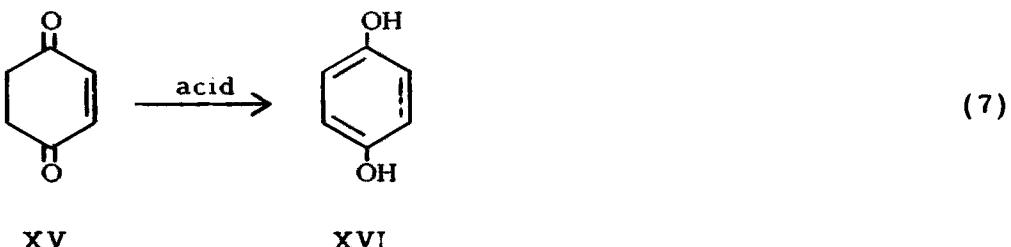
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has been isolated and found (Ref 8) to revert to the aromatic hydroquinone (XVI) upon treatment with acid. Accordingly, compound XIII was treated with boron



trifluoride etherate and the infrared spectrum of the solution was examined at intervals. No signs of either an aromatic ring or an N-H bond could be detected. The spectral region containing absorptions due to N-F bonding was obscured by absorptions of the reagent. A brown-black insoluble product gradually appeared and the disappearance of the 238-240  $\mu$  band in the ultraviolet indicated that the bis(fluorimine) was being consumed

#### E. SYNTHESIS AND PURIFICATION OF t-BUTYLDIFLUORAMINE

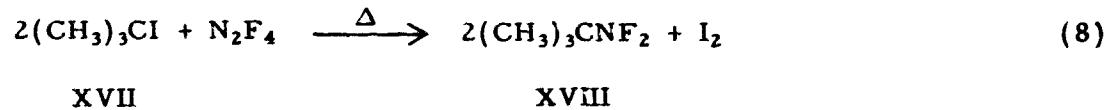
In the course of earlier studies on the reactions of t-butyldifluoramine (Ref 9, 10 and 11), an improved method for the synthesis of this model compound was developed. A paper describing the synthesis has been prepared for publication (Ref 7) and cleared for release. Due to the high volatility of the compound, however, satisfactorily precise analytical data have not yet been obtained. Improved analytical techniques have now been devised and the synthesis of a new sample of t-butyldifluoramine was undertaken.

The thermally initiated reaction of tetrafluorohydrazine with t-butyliodide (Ref 7) was repeated and the product was purified by trap-to-trap distillation

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under vacuum followed by a fractional distillation at atmospheric pressure (bp 55 to 57°C). The last traces of iodine were not removed, however, and the analytical results were not adequate for publication. Attempts at further purification resulted in the loss of the entire sample, necessitating an additional preparation. The product obtained in the latter run is being purified entirely by trap-to-trap distillation.

— 11 —  
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Task 51  
Report RMD 5043-Q3-64

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### III. EXPERIMENTAL

#### A. 1,1-BIS(DIFLUORAMINO)HEPTANE

Difluoramine was generated in the usual manner (Ref 12) by the acid hydrolysis of 0.28 mole of difluorourea. The dried gas was passed into a 1-liter flask containing 5 ml of 105% fuming sulfuric acid and fitted with a Dry Ice condenser. After all the difluoramine had been collected under reflux, a solution of 6.0 gm (0.053 mole) n-heptanal (Eastman) in 18 ml of Freon-113 was added slowly at 0°C. After the mixture was stirred for 4 hours at 0 to 5°C and flushed with nitrogen, it was diluted with water and separated. The organic layer was combined with a methylene chloride wash of the aqueous layer, dried, and stripped of solvent. Distillation of the residue gave 4.30 gm (0.0213 mole, 40.5%) of 1,1-bis(difluoramino)heptane (bp 58.5 to 59.0°C/13.0 mmHg) in addition to 0.75 gm (0.0024 mole, 9.0%) of bis(1-difluoraminoethyl)ether (bp 93 to 95°C/0.1 mmHg). Two repetitions of the above procedure yielded an additional 2.15 gm of gem-compound which was combined with the above and distilled (bp 64.5 to 65.0°C/17.3 mmHg;  $n_{D}^{20} = 1.3861$ )

Anal. Calcd: C, 41.58; H, 6.98; N, 13.85  
Found: C, 41.86; H, 7.14; N, 13.34.

The product was redistilled twice more, discarding a larger forecut in the final distillation.

Anal. Calcd: C, 41.58; H, 6.98; N, 13.85  
Found: C, 42.18; H, 6.86; N, 13.48.

#### B. ETHYL-N-CYCLOHEXYLCARBAMATE

In a 1-liter flask was placed a large magnetic stirring bar, 50 ml water, 150 gm of crushed ice, and 100 gm (1.01 moles) of cyclohexylamine (Matheson Coleman and Bell, bp 133 to 135°C). The flask was surrounded by an ice bath and cooled to 3°C. Ethyl chloroformate (113.8 gm, 1.05 moles, Matheson Coleman and Bell, bp 93 to 95°C) was placed in a dropping funnel and one-half was added dropwise at a rate which allowed the reaction mixture to be maintained at 8 to 12°C (required 45 min). From a second dropping funnel a chilled solution

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of 43 gm (1.09 moles) of NaOH in 150 ml water was added concurrently with the second half of the ethyl chloroformate over a 45 minute period. The mixture was stirred for 30 minutes at 10 to 12°C. The solid product was then collected by filtration, washed with 1500 ml water at 10 to 15°C, and dried under vacuum. A yield of 164.6 gm (95.5%) of carbamate, mp 52 to 54.5°C, was obtained (Lit. mp 56°C, Ref 5; 56 to 58°C, Ref 6).

#### C. CYCLOHEXYLDIFLUORAMINE

In a 1-liter flask equipped with a large magnetic stirring bar, 68.5 gm (0.40 mole) of ethyl-N-cyclohexylcarbamate (mp 52 to 54.5°C) was suspended in 700 ml of distilled water. The flask was cooled in an ice bath and maintained at 5 to 8°C for four hours while 0.88 mole of fluorine, diluted to 20% with nitrogen, was introduced. During the reaction the finely divided solid gradually coagulated to a pasty mass. Work-up of the crude product is in progress.

#### D. t-BUTYLDIFLUORAMINE

To each of two 2-liter bulbs was charged 6.00 gm (0.031 mole) of t-butyl iodide (K and K Laboratories, washed with aqueous thiosulfate and dried) and 0.040 mole of tetrafluorohydrazine. The bulbs were heated to 80°C over a six-hour period and then allowed to cool to room temperature. The volatile contents of both bulbs were distilled under vacuum at room temperature to a U-trap at -78°C. The trap-to-trap distillation was repeated three additional times, with the vapors passing over crystalline sodium thiosulfate and Drierite during the last two passes. The resulting product, although colorless, developed a transient yellow-brown color on exposure to air, indicating that it contained dissolved tetrafluorohydrazine.

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#### IV. FUTURE WORK

During the next quarter our research effort will be devoted to the following areas:

- Identification of the product resulting from the elimination of two equivalents of HF from 1, 1-bis(disfluoramino)heptane.
- Development of a synthesis of 1-difluoramino-1-fluoriminoheptane.
- Exploration of the addition reactions of the double bond in a trifluoroamidine.
- Dehydrofluorination of cyclohexyldifluoramine.
- Exploration of the addition and carbonyl-type reactions of cyclohexylidene-fluorimine.

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**Section II**

**Task 52**

**SYNTHESIS OF COMPOUNDS FOR STRUCTURE-SENSITIVITY STUDY**

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Section II

SYNTHESIS OF COMPOUNDS FOR STRUCTURE-SENSITIVITY STUDY

A. P. Kotloby

Report RMD 5043-Q3-64

RMD Project 5043, Task 52  
Report Period: 1 July 1964 to  
30 September 1964

Contract No. NOnr 4364(00)  
ARPA Order No. 417  
Project Code 4910

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**FOREWORD**

This section of the quarterly progress report describes the work carried out during the period from 1 July 1964 to 30 September 1964 on the synthesis of organodifluoramines for use in the study of structure-sensitivity relationships.

The following personnel contributed to this effort: D. D. Perry (Section Supervisor), A. P. Kotloby (Project Scientist), W. H. Wieting (Synthesis), R. N. Storey, D. Z. Chowanec and D. N. Pregler (Instrumental and Chemical Analysis).

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CONTENTS

	Page
I. INTRODUCTION	1
II. DISCUSSION	2
A. Synthesis of Tris(difluor amino)methoxyalkanes	2
B. Synthesis of Bis(difluor amino)alkanes	6
III. EXPERIMENTAL	7
A. Synthesis of Tris(difluor amino)methoxypentane	7
B. Synthesis of 1,1-Bis(difluor amino)cyclohexane	7
IV. FUTURE WORK	9
V. REFERENCES	10

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Task 52  
Report RMD 5043-Q3-64

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## ILLUSTRATIONS

Figure		Page
1	Infrared Spectrum of 1,1-Bis(difluoramino)cyclohexane	7
2	Gas Chromatogram of 1,1-Bis(difluoramino)cyclohexane	8

## TABLES

Table		Page
I	Conditions Investigated for Gas Chromatographic Purification of Tris(difluoramine)methoxypentane	5

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## I. INTRODUCTION

This portion of the advanced oxidizer research program deals with the synthesis phase of a study aimed at an understanding of the structural and chemical factors affecting the sensitivity of organic difluoramines. One of the principal problems involved in the use of these compounds in propellant formulations is their sensitivity to stresses such as heat and mechanical shock. The evaluation of sensitivity data gathered from a sufficiently large number of organodifluoramines, representing a variety of structural types and functional groups, could be useful in guiding research toward the synthesis of compounds having a minimum degree of sensitivity in relation to their energy content.

In accordance with this goal, Thiokol Chemical Corporation, Reaction Motors Division, has undertaken the task of preparing a variety of organic difluoramines for sensitivity evaluation by the Naval Ordnance Laboratory, White Oak, Silver Spring, Maryland. These compounds have been selected on a systematic basis to provide information concerning the effect on sensitivity of such factors as the NF<sub>2</sub>-to-carbon ratio, the type of NF<sub>2</sub> substitution, and the presence of various organofunctional groups. The sensitivity of these compounds is being measured by the thermal explosion delay (Wenograd) test (Ref 1). Some of these data obtained on N-F materials have been described by Rosen *et al.* (Ref 2) and presented at the Second Sensitivity Seminar (Ref 3). These results show some interesting and potentially valuable correlations between vicinally and geminally substituted organo-bis(difluoramines). This work has been extended to include the study of highly energetic tris(difluoramino)methoxy derivatives which are produced via addition reactions of perfluoroguanidine with alcohols. Our efforts in the current quarter have been directed toward the synthesis of tris-NF<sub>2</sub> derivatives and finding methods of purifying them to > 99%, as well as to the synthesis of vicinal and geminal bis(difluoramino)alkanes as requested by the Naval Ordnance Laboratory.

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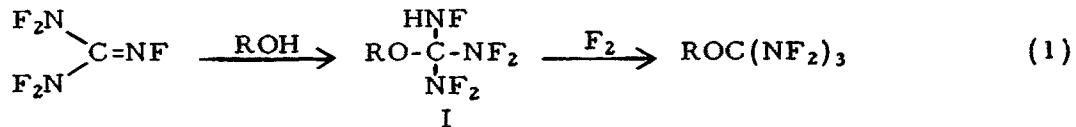
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## II. DISCUSSION

The basic considerations in the selection of compounds to be investigated on this program have already been discussed in previous reports (e.g., Ref 4). During the past quarter, efforts have been directed toward two areas: (1) the preparation and purification of a typical tris- derivative, tris(difluoramino)methoxypentane; and (2) the preparation of certain bis(difluoramino)-alkanes needed for a study being conducted at the Naval Ordnance Laboratory.

### A. SYNTHESIS OF TRIS(DIFLUORAMINO)METHOXYALKANES

Tris(difluoramino)methoxypentane are prepared by the nucleophilic addition of alcohols to perfluoroguanidine followed by the fluorination of the resulting fluoramino adduct (Ref 5, 6 and 7):



We have previously synthesized and attempted to purify a series of tris(difluoramino)methoxypentane from primary C<sub>4</sub>-C<sub>9</sub> alcohols and from a limited number of secondary alcohols (Ref 8) using the sequence of reactions shown in equation 1. When difficulties were encountered in purifying these materials, tris(difluoramino)methoxypentane was used as a model compound for finding the optimum conditions for purification by the gas chromatographic technique.

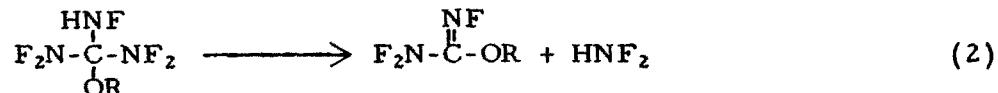
The fluoramino adduct (I), obtained in 80-90% yield, could be distilled without decomposition under reduced pressure, but had only a limited stability when stored at 0 to 5°C in a glass container. The infrared spectra of freshly prepared material showed, in addition to N-F absorptions (10.3, 11.1, 11.6μ), strong absorptions at 3.04μ corresponding to the N-H stretching. A partially decomposed sample showed the presence of the >C=N bond at 5.96-6.10μ.

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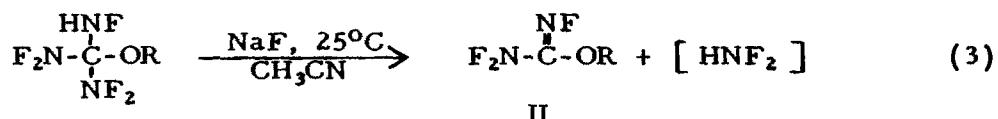
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[ King (Ref 9) gives  $6.11\mu$  for the position of the  $\text{C}=\text{N}$  absorption in  $\text{p}-\text{CH}_3\text{C}_6\text{H}_4\text{N}=\text{C}-\text{N}(\text{CH}_3)_2$  ], indicating that some elimination of difluoramine had taken place:



The bis(difluoramino)fluoraminomethoxy derivative was fluorinated at  $0^\circ\text{C}$  with 6% fluorine in nitrogen. Acetonitrile is the preferred solvent for the reaction since it gives less fluorination of the alkyl chain. The use of NaF as an HF scavenger in the fluorination step produced an exothermic reaction accompanied by gas evolution, giving a nearly quantitative yield of colorless liquid, which was identified as the fluorimino derivative (II).



The structure of the product was established by its infrared and NMR spectra. In the case of difluoraminofluoriminomethoxyheptane, we observed that the product consisted of a 3:2 mixture of syn- and anti-isomers. The NMR data are shown below:

syn:  $-37.3 \delta (\text{NF}_2) + 51.4 \delta (\text{C}=\text{NF})$

anti:  $-42.6 \delta (\text{NF}_2) + 43.4 \delta (\text{C}=\text{NF})$

( $\delta$  = parts per million from  $\text{CFCl}_3$  reference.)

Elimination of NaF from the reaction did not completely prevent the formation of the fluorimino derivative, but it reduced the extent of it sharply.

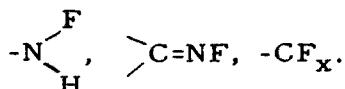
Based on NMR measurements, the crude reaction product from the fluorination step assayed 80-90% of tris(difluoramino)methoxyalkane. Impurities

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containing the following functional groups have been identified by infrared and NMR spectroscopy:



The probable structures of these impurities are shown below:



(where  $\text{R}_f$  = partially fluorinated alkyl chain).

Work is currently in progress on the isolation and characterization of the major impurities in the tris (difluoramine)methoxypentane by means of vapor phase chromatography.

Our initial efforts to obtain very pure samples of tris(difluoramino) compounds were frustrated by difficulties encountered in gas chromatographic purification. The reasons for these difficulties are the presence of a considerable number of contaminants, together with the apparent instability of the tris-compounds in the chromatographic columns that were used. To determine gas chromatographic parameters, work was carried out on a single compound, tris(difluoramino)methoxypentane. The types of columns and experimental conditions employed are summarized in Table I. The most encouraging results so far were obtained with Halocarbon Oil on Fluoropak. This is an inert substrate and points up the fact that decomposition on the column is one of the most serious problems in this work. Currently, this type of column is being used to separate larger quantities of the crude product that had been distilled through the short column under vacuum, so that the distillation temperature is not greater than 50-60°C.

In every case where some separation of the reaction mixture was indicated, a change to a larger, preparative size column (12 to 20 ft x 3/8 in.) for the purpose of purifying a large sample, resulted in poorer separation or the loss of the sample on the column. It would be desirable also to decrease the retention times, which are 2-3 hours at 80°C; however, increasing the column temperature to 115°C led to the decomposition of the sample. Additional work will be needed in order to establish the optimum parameters for separating these mixtures by gas chromatography.

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TABLE I

CONDITIONS INVESTIGATED FOR GAS CHROMATOGRAPHIC  
PURIFICATION OF TRIS(DIFLUORAMINO)METHOXYPENTANE

<u>Column</u> <u>(Cu tubing passivated with F<sub>2</sub>)</u>	<u>Column Temp</u> <u>(°C)</u>	<u>Remarks</u>
6 ft x 3/8 in.; 20% SF-96 a-w Chromosorb P	130	Two major unresolved peaks
6 ft x 3/8 in.; 20% SF-96 a-w Chromosorb P	75	Poor resolution; some decomposition
3 ft x 1/4 in.; 20% SF-96 a-w Chromosorb P	75	Poor-to-good resolution but only with < 5 $\mu$ l injection
6 ft x 1/4 in.; 20% Kel-F Oil a-w Chromosorb P	75	Very broad, unresolved peaks
6 ft x 14 in.; 20% Halocarbon Oil 14-25 a-w Chromosorb P	80	Fair separation of 3-5 peaks Resolution needs to be improved
6 ft x 1/4 in.; 20% SF-96 a-w Chromosorb W	80	No resolution
6 ft x 1/4 in.; 20% SF-96 HMDS Chromosorb P	80	Broad peaks, indication of decomposition on column
6 ft x 1/4 in.; 20% Halocarbon Oil 14-25; Fluoropak 80	60-90	Fair but not always reproducible resolution; occasional indication of decomposition of column

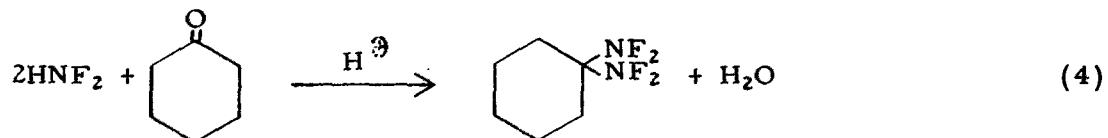
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### B. SYNTHESIS OF BIS(DIFLUORAMINO)ALKANES

Work was also carried out on the synthesis of vicinal and geminal adducts which had been requested by the Naval Ordnance Laboratory. Approximately 18 g of crude 1,1-bis(difluoramino)cyclohexane was prepared by the well-known reaction (Ref 10):



After gas chromatographic purification, 5.2 g of 1,1-bis(difluoramino)cyclohexane was obtained:  $b_{10}$  46.0°C,  $n_D^{25}$  1.4062.

The best purification was obtained by using a 12 ft x 1/4 in. copper column with 20% Halocarbon Oil 14-25 on Fluoropak 80. Prior to making the column, the copper tubing was passivated with fluorine. At a column temperature of 105°C or higher, the chromatogram consisted of two major peaks, the first being larger than the second. By gradually decreasing the column temperature, the area under the second peak increased and that under the first peak decreased until at 60°C the first peak became insignificant. An analysis of the second peak (which was the only major peak at 60°C) showed it to be 1,1-bis(difluoramino)cyclohexane. This indicates that at higher temperatures the gem-adduct decomposes on column. No determinations have yet been made of the nature of the decomposition products. We also found that if we used an identical chromatographic column, but one through which were first made several passes of crude tris(difluoramino)methoxyalkane, the retention time of 1,1-bis(difluoramino)cyclohexane at 60°C was approximately six times longer than in the column which had not been exposed to tris-NF<sub>2</sub> adducts. This, together with the fact that chromatograms of tris(difluoramino)methoxyalkanes are highly complex and poorly reproducible, further suggests that tris-NF<sub>2</sub> compounds decompose on the column.

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### III. EXPERIMENTAL

#### A. SYNTHESIS OF TRIS(DIFLUORAMINO)METHOXYPENTANE

The experimental conditions and the setup were the same as described in the previous report (Ref 8).

#### B. SYNTHESIS OF 1,1-BIS(DIFLUORAMINO)CYCLOHEXANE

The experimental conditions and the setup were the same as described in our previous report (Ref 10). The distillation of 18 g of crude product gave 16.3 g (83% average yield of four runs) of 1,1-bis(difluoramino)cyclohexane, which after gas chromatographic purification, had the following constants:  $b_{10}$  46.0°C,  $b_{760}$  164.0°C,  $n_D^{25}$  1.4062. The infrared spectrum and the chromatogram are shown below.

Anal. Calcd. for  $C_6F_4H_{10}N_2$ : C, 38.71; H, 5.41; N, 15.05.

Found: C, 38.71  $\pm$  0.16; H, 5.59  $\pm$  0.12; N, 15.03  $\pm$  0.11.

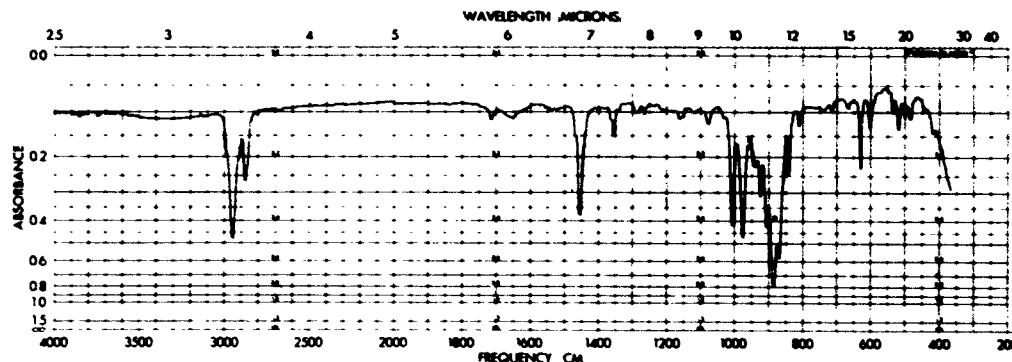


Figure 1. Infrared Spectrum of 1,1-Bis(difluoramino)cyclohexane

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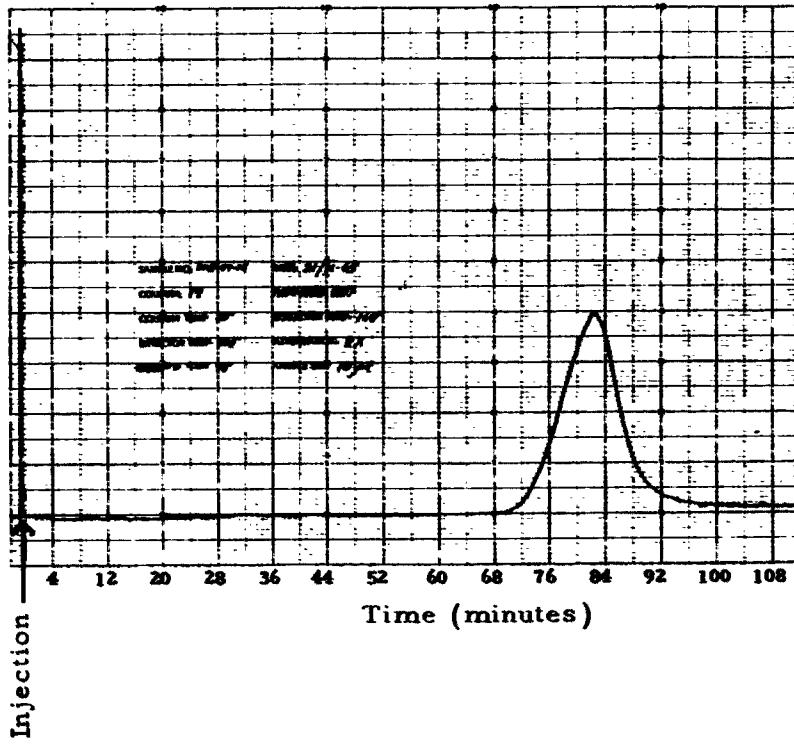


Figure 2. Gas Chromatogram of 1,1-Bis(difluoramino)cyclohexane

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#### IV. FUTURE WORK

During the next quarter, the following compounds will be prepared in amounts of 5 g or more and of >99% purity:

Ethyl 2, 3-Bis (difluoramino)propionate  
1, 1-Bis (difluoramino)heptane  
2, 2-Bis (difluoramino)heptane  
1, 2-Bis (difluoramino)heptane  
1, 1-Bis (difluoramino)-1-phenylethane  
1, 2-Bis (difluoramino)-1-phenylethane  
Phenyl-bis (difluoramino)methane.

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Section III

Task 53

CHEMISTRY OF THE OXYGEN SUBFLUORIDES



### Section III

## CHEMISTRY OF THE OXYGEN SUBFLUORIDES

S. I. Morrow  
A. R. Young

Report RMD 5043-Q3-64

RMD Project 5043, Task 53  
Report Period: 1 July 1964 to  
30 September 1964

Contract No. NOnr 4364(00)  
ARPA Order No. 417  
Project Code 4910

## FOREWORD

This section of the report summarizes the results of studies of the chemistry of dioxygen difluoride, trioxygen difluoride, and of dioxygenyl salts during the period from 1 July 1964 to 30 September 1964. This program was monitored by Mr. R. Hanson of the Office of Naval Research.

Personnel contributing to these studies were: A. R. Young (Project Supervisor), S. I. Morrow (Principal Investigator), K. Tiger, J. Crothamel, R. Storey, and R. Crooker.

CONTENTS

	Page
I. INTRODUCTION	1
II. DISCUSSION	2
A. Reactions of Dioxygen Difluoride	2
B. Reactions of Trioxygen Difluoride	7
C. Reactions of Dioxygenyl Salts	8
III. EXPERIMENTAL	12
A. Reactions of Dioxygen Difluoride	12
B. Reactions of Trioxygen Difluoride	15
C. Reactions of Dioxygenyl Salts	16
IV. FUTURE WORK	17
V. REFERENCES	18

## ILLUSTRATIONS

Figure		Page
1	Infrared Spectrum of $O_2F_2$ -CsCl Product (KBr Pellet)	5
2	Infrared Spectrum of $O_2F_2$ -CsCl Product (Kel-F mull)	5

## TABLES

Table		Page
I	Reactions of $O_2F_2$ with CsCl	3
II	Elemental Composition of $O_2F_2$ -CsCl Solid Product	3
III	Principal Diffraction Lines of Hexafluoroarsenates	9

## I. INTRODUCTION

This program is concerned with a study of the chemistry of the oxygen subfluorides,  $O_2F_2$ ,  $O_3F_2$  and  $O_4F_2$ , with the objective of discovering routes to stable derivatives of the subfluorides which may be of value as energetic solid oxidizers.

During the past quarter we continued our efforts to prepare new interhalogen and oxyhalogen molecules and ions via reactions of  $O_2F_2$  with such substrates as  $CsClF_4$ ,  $CsCl$ , and  $BrF_5$ . We have also explored reactions of  $O_3F_2$  with radicals in the hopes of detecting coupling products and have initiated a study of coupling reactions of the radical ion,  $\cdot O_2^+$ .

In our last quarterly report (Ref 1) we stated that efforts to prepare new dioxygenyl salts were to be discontinued because of the apparent instability of the  $O_2^+$  in HF. Since that time we have performed a calculation which shows that the heat of formation of the hypothetical ionic salt,  $O_2^+ClO_4^-$ , would be of the same order of magnitude as that of the known compound,  $NO_2ClO_4$ . As a result we feel that further efforts in the area of dioxygenyl salt synthesis are warranted.

## II. DISCUSSION

### A. REACTIONS OF DIOXYGEN DIFLUORIDE

The reactions of  $O_2F_2$  with  $CsCl$ ,  $CsClF_4$ , and  $BrF_5$  were investigated as possible routes to new interhalogen and oxyhalogen molecules or ions. In addition, the preparation of an arsenic pentafluoride adduct of  $Cl_2O$  was carried out as reported by M. Schmeisser (Ref 2) as a preliminary step in the study of the action of  $O_2F_2$  on  $ClO \cdot AsF_5$ .

#### 1. Reaction of $O_2F_2$ with $CsCl$

The objective of studying the reaction of  $O_2F_2$  with  $CsCl$  is to determine whether a hypothetical complex oxyhalogen anion,  $F_2ClO_2^-$ , can be stabilized by the large cesium cation. Such an anion would most likely have a peroxy ( $-Cl-O-O-$ ) structure and could be formed as shown in equation (1).



To date our results present no positive evidence for formation of a product having the composition,  $CsClF_2O_2$ . However, there is considerable evidence that the solid product contains a component having properties inconsistent with those of known solids that are likely to result from a reaction of  $O_2F_2$  with  $CsCl$ , such as  $CsF$ ,  $Cs_2O$ , and  $CsClF_4$ .

A series of six runs were carried out with  $CsCl$  and excess  $O_2F_2$  under conditions which are summarized in Table I. The results of elemental analysis of samples of the solid products of two of these runs are presented in Table II. These show a  $Cs:Cl:F$  ratio of 1:0.5:1. With the exception of the oxygen content (obtained by difference) the analytical results are in excellent agreement with theory for a composition  $CsClO_2F \cdot CsF$  ( $Cs:Cl:O:F = 1:0.5:1:1$ ). In support of the existence of such an anion ( $FClO_2^-$ ) it was observed that the solid product attacks glass. X-ray patterns obtained on samples sealed in Pyrex capillaries were found to be identical to the pattern exhibited by  $Cs_2SiF_6$ . On the other hand, aqueous solutions of the solid were only mildly oxidizing toward KI.

TABLE I  
REACTIONS OF  $O_2F_2$  WITH CsCl

<u>Experiment Number</u>	<u>CsCl (gm)</u>	<u>Diluent</u>	<u>Temperature (°C)</u>	<u>Product (gm)</u>	<u>Color of Product</u>
1	0.5736	none	-110 to -78	0.6075	white
2	2.4171	none	-110 to -78	2.4330	yellow
3	1.6494	$C_3F_8$	-110 to -78	1.7514 <sup>a</sup>	yellow
4	0.6257 <sup>a</sup>	$C_3F_8$	-78	0.6212	yellow
5	0.6260	none	-106 to -78	0.6383	yellow
6	0.9750	none	-100	b	b

a - Some of the product from experiment 3 was ground and used in experiment 4  
b - Experiment still in progress

TABLE II  
ELEMENTAL COMPOSITION OF  $O_2F_2$ -CsCl SOLID PRODUCT

Element (%)	CsCl Reagent	Found		Calculated for			
		Product Run No.1	Product Run No.4	CsCl	CsF	$Cs_2O$	$CsClO_2F \cdot CsF$
Cs	79.22	67.54	71.34	78.92	87.50	94.32	71.59
Cl	21.42	8.84	8.75	21.08	---	---	9.56
F	---	10.60	11.60	---	12.50	---	10.23
O	---	13.02*	8.31*	---	---	5.68	8.62
Atomic Ratios	Cs:Cl 1:1	a	b	Cs:Cl 1:1	Cs:F 1:1	Cs:O 1:2	Cs:Cl:F:O 1:0.5:1.1:1

\*By difference      a - Cs:Cl:F:O  
                          1:0.5:1.1:1.6      b - Cs:Cl:F:O  
                          1:0.5:1.1:1

Infrared spectra of the  $O_2F_2$ -CsCl product (Figures 1 and 2) shed little light on the composition of the material. These spectra were obtained on a KBr pellet (Figure 1) and by mulling the solid in a Kel-F oil (Figure 2). Both show strong absorptions at approximately  $1235\text{ cm}^{-1}$  and between  $1400-1550\text{ cm}^{-1}$  which are the regions of absorption of  $NO_2^-$  and  $NO_3^-$  ions. However, qualitative tests show the absence of significant nitrate and nitrite impurities. The spectrum shown in Figure 2 has an absorption at  $725\text{ cm}^{-1}$  attributable to  $SiF_6^=$ . The presence of this band is due to reaction of the sample with a Pyrex vial in which it was stored prior to infrared analysis. When the solid was not allowed to contact glass, the band at  $725\text{ cm}^{-1}$  did not appear (Figure 1).

Although the evidence that a new oxidizing anion is present in the solid product of the  $CsCl-O_2F_2$  reaction is not unequivocal, it is believed that the reactivity of this material toward glass (indicating covalent fluorine bonding) is sufficient justification for further examination of this reaction. Attempts will be made to determine whether we are dealing with a unique reaction product by comparing the results of the reaction of  $O_2F_2$  with CsCl with those of a reaction of CsCl with an equimolar mixture of  $O_2$  and  $F_2$ . In addition, further studies of the chemical and physical properties of the  $O_2F_2$ -CsCl product will be conducted in order to determine whether an active fluorine species is truly present.

## 2. Attempted Reaction of $O_2F_2$ with $CsClF_4$

The reaction between  $CsClF_4$  and  $O_2F_2$  was investigated to determine whether the  $ClF_6^-$  ion might be prepared (equation 2).  $CsClF_4$  was allowed to contact successive samples of freshly generated  $O_2F_2$  over a period of several hours. No change in the x-ray pattern of the  $CsClF_4$  was detected after this treatment.



## 3. Attempted Reaction of $O_2F_2$ with $BrF_5$ under Pressure

The reaction between  $O_2F_2$  and  $BrF_5$  was attempted in a vacuum apparatus at  $-78^\circ C$  during the previous quarter (Ref 1), but no positive results were obtained. An attempt was made to carry out this reaction during the current quarter under high pressure conditions and at a temperature higher than  $-78^\circ C$ . It was thought that  $O_2F_2$  might have sufficient fluorinating activity under these conditions to convert  $BrF_5$  to  $BrF_7$ . A small metal tube was assembled to carry out this reaction. However, it was found that  $O_2F_2$  decomposed too rapidly, even at  $-78^\circ C$ , to permit its efficient transfer from the generator to the metal reactor at  $-196^\circ C$ . Although  $O_2F_2$  can be transferred at  $-78^\circ C$  under special

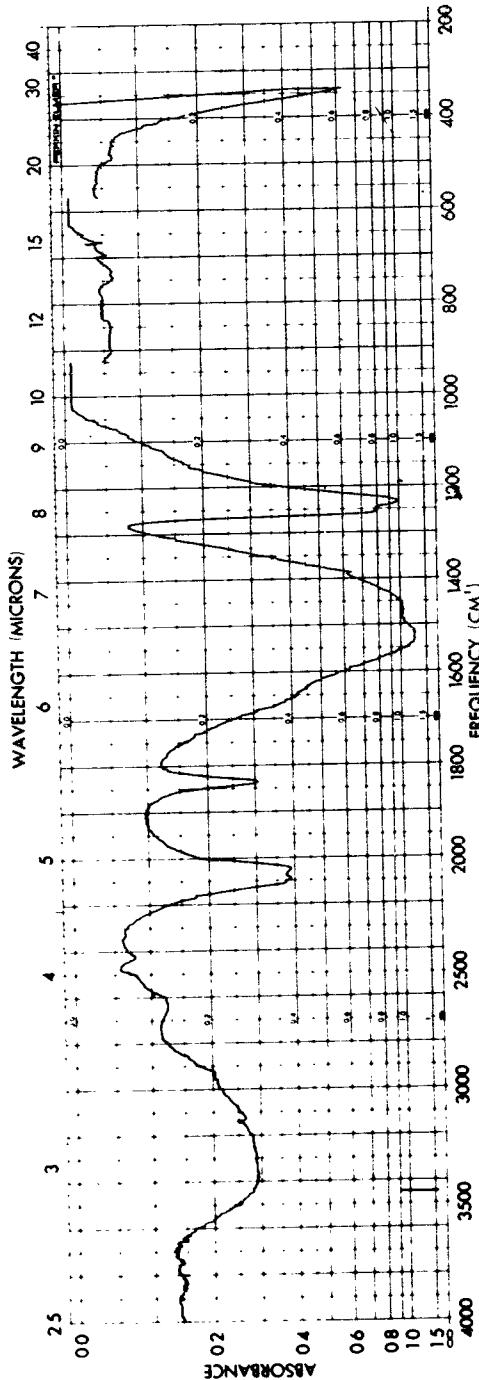


Figure 1. Infrared Spectrum of  $O_2F_2$ -CsCl Product (KBr Pellet)

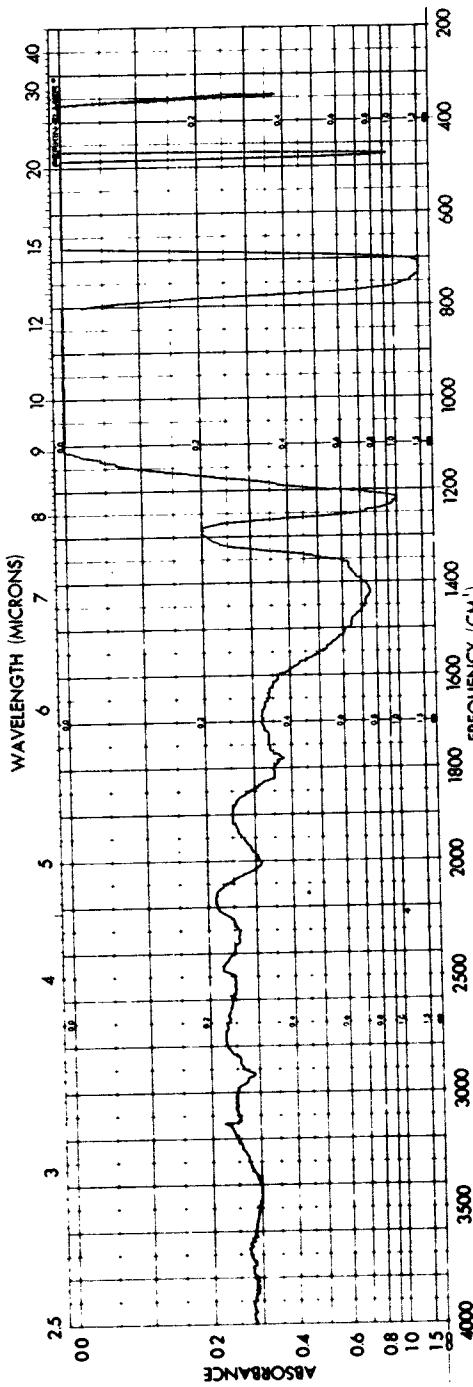


Figure 2. Infrared Spectrum of  $O_2F_2$ -CsCl Product (KBr-F mull)

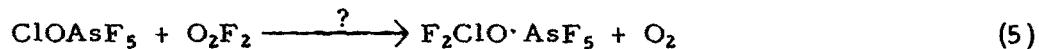
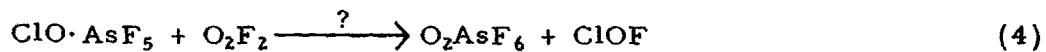
conditions, the geometry of the reactor used here was evidently unfavorable. Consequently, redesign of the reactor would be required in order to carry out this experiment.

#### 4. Preparation of $\text{ClO}\cdot\text{AsF}_5$

Schmeisser and Brandle (Ref 2) have reported the synthesis of a 1:1 adduct of  $\text{Cl}_2\text{O}$  with  $\text{AsF}_5$  which decomposes at  $-50^\circ\text{C}$  to yield  $\text{ClO}\cdot\text{AsF}_5$  (equation 3).

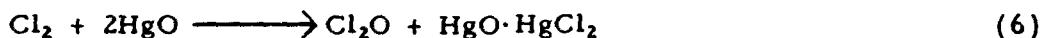


No information about the stability of  $\text{ClO}\cdot\text{AsF}_5$  is given in the paper referenced. It would be extremely interesting to observe the action of  $\text{O}_2\text{F}_2$  on this adduct of chlorine monoxide. Reactions might occur as shown in equations 4 and 5, producing new oxyhalogen species. It was therefore decided to repeat the preparation



of the  $\text{Cl}_2\text{O}\cdot\text{AsF}_5$  claimed by Schmeisser in order to observe its conversion to  $\text{ClO}\cdot\text{AsF}_5$  and to ascertain the stability of the latter adduct. Once the stability of  $\text{ClO}\cdot\text{AsF}_5$  is known an experiment can be designed in which the adduct is allowed to contact  $\text{O}_2\text{F}_2$  under the best possible conditions to effect reactions as indicated in equations 4 and 5.

$\text{Cl}_2\text{O}$  was prepared by the reaction of chlorine (equation 6) with excess  $\text{HgO}$  suspended in Freon 11 ( $\text{CFCl}_3$ ). The solution of  $\text{Cl}_2\text{O}$  in Freon 11 was isolated by distillation and treated with  $\text{AsF}_5$  at  $-80^\circ\text{C}$ . A white precipitate,



presumably  $\text{Cl}_2\text{O}\cdot\text{AsF}_5$  (equation 3), formed immediately at that temperature. The system was pumped while being maintained at  $-80^\circ\text{C}$  in order to remove unreacted  $\text{AsF}_5$ ,  $\text{Cl}_2\text{O}$ ,  $\text{Cl}_2$  and the solvent. The conversion of the solid  $\text{Cl}_2\text{O}\cdot\text{AsF}_5$  to  $\text{ClO}\cdot\text{AsF}_5$  is presently being studied.

## B. REACTIONS OF TRIOXYGEN DIFLUORIDE

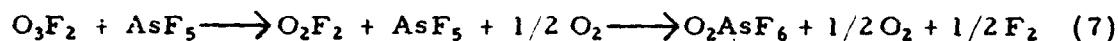
We have discussed previously the desirability of undertaking a study of the chemistry of  $O_3F_2$  and have described the manner in which we have prepared relatively pure samples of this material (Ref 1). During the past quarter we explored some reactions of  $O_3F_2$  under conditions that would permit only relatively stable products to be detected. The reagents examined included those with  $Cl_2$ ,  $AsF_5$ ,  $NO$  and  $CsClF_4$ .

### 1. Reaction of $O_3F_2$ with $Cl_2$

$O_2F_2$  reacts with chlorine to form a purple intermediate which reportedly has the composition  $(O_2ClF_3)_n$  (Ref 3) and which decomposes above  $-78^\circ C$  to yield  $O_2$  and  $ClF_3$ . An analogous reaction was attempted with  $O_3F_2$  at  $-160^\circ C$  in an all glass system. In this case there was only a trace of purple material observed in the reactor. The ultimate gaseous products formed (in addition to oxygen and fluorine) were  $ClO_2$ ,  $ClO_2F$ , and  $ClO_3F$ . No evidence of intermediate adduct formation was obtained. However, further study of both the  $Cl_2-O_2F_2$  and  $Cl_2-O_3F_2$  systems by low temperature infrared techniques is planned for the near future in order to detect the formation of metastable products.

### 2. Reaction of $O_3F_2$ with $AsF_5$

$O_3F_2$  was mixed with  $AsF_5$  at  $-160^\circ C$  and the mixture was allowed to remain at that temperature for 1.5 hours. Upon warming to room temperature noncondensable decomposition gases and a white solid were present in the reactor. X-ray analysis showed the solid to be  $O_2AsF_6$ . The reaction probably occurred as shown in equation (7).



### 3. Reaction of $O_3F_2$ and $NO$

No volatile reaction products could be detected in a mixture of  $O_3F_2$  and  $NO$  at  $-196^\circ C$  or at  $-185^\circ C$ . When the system was warmed to  $-78^\circ C$ ,  $NO_2$  was formed. This reaction, like the reaction with  $Cl_2$ , will be studied further by low temperature infrared techniques.

#### 4. Attempted Reaction of $O_3F_2$ with $NONF_2$

An attempt was made to study possible free radical coupling between paramagnetic  $O_3F_2$  and the unstable adduct of NO with  $N_2F_4$ . Unfortunately, just as the purple  $NONF_2$  adduct had been condensed onto  $O_3F_2$  at  $-196^{\circ}C$ , the reactor cracked and the experiment had to be abandoned. Further study of this system will be carried out at a later date when a low temperature infrared cell has been assembled.

#### 5. Reaction of $O_3F_2$ with $CsClF_4$

As in the case of the attempted reaction of  $O_2F_2$  with  $CsClF_4$ , we had hoped that  $O_3F_2$  would fluorinate the  $ClF_4^-$  anion. After treatment of  $CsClF_4$  with  $O_3F_2$  at  $-107^{\circ}C$  for several hours, the system was raised to room temperature and a sample of the residual solid was subjected to X-ray analysis. The diffraction pattern indicated the presence of unreacted  $CsClF_4$  and  $Cs_2SiF_6$ .

### C. REACTIONS OF DIOXYGENYL SALTS

Since the dioxygenyl ion has an odd number of electrons, it is not surprising that paramagnetism has been observed in dioxygenyl salts (Ref 4). The reaction of dioxygenyl salts with radicals or atoms (equation 8) might lead to the synthesis of new cations and covalent peroxy compounds. This concept was tested during the past quarter by attempting a coupling reaction between  $\cdot NF_2$  radicals and dioxygenyl hexafluoroarsenate.



#### 1. Reaction of $O_2AsF_6$ with Difluoramino Radicals

$NF_2$  radicals were generated by passing  $N_2F_4$  through a hot metal tube in a vacuum. The radicals were condensed directly onto a sample of  $O_2AsF_6$  held at  $-196^{\circ}C$ . When the system was allowed to stand at  $-196^{\circ}C$ , no volatile materials, such as  $O_2$ , were evolved. The system was brought up to  $-117^{\circ}C$  and kept at this temperature for an hour. Again no volatile materials were evolved. However, when the mixture was allowed to warm to room temperature,  $NF_3$  and oxygen, as well as minor amounts of  $NO_2$  and  $N_2$ , were detected. The solid residue, which showed no visible evidence of having undergone a change, was not that of pure  $O_2AsF_6$ . Its X-ray diffraction pattern, as well as those of  $O_2AsF_6$ , and other possible products are given in Table III. We are unable to identify the

the product on the basis of its X-ray pattern alone. When the product was stored in a Kel-F vial in the dry-box prior to further analysis, it began to volatilize. After 5 days only a small amount was left. Further work with the remainder of this product, as well as a quantitative study of the  $\cdot\text{NF}_2\text{-O}_2\text{AsF}_6$  reaction will be carried out during the next quarter.

TABLE III  
PRINCIPAL DIFFRACTION LINES OF HEXAFLUOROARSENATES

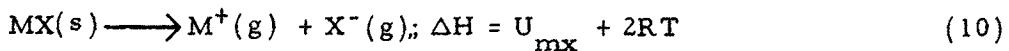
$\text{NF}_2\text{-O}_2\text{AsF}_6$ Product		$\text{O}_2\text{AsF}_6\text{-NOASF}_6$		$\text{N}_2\text{F}_4(\text{AsF}_5)_x$		$\text{NO}_2\text{AsF}_6$	
<u>d(Å)</u>	<u>I</u>	<u>d(Å)</u>	<u>I</u>	<u>d(Å)</u>	<u>I</u>	<u>d(Å)</u>	<u>I</u>
4.68	M	4.60	S	5.37	M	4.99	W
4.03	S	4.00	S	4.46	S	4.57	W
3.54	S	2.84	M	3.39	S	4.42	M
2.85	M	2.32	W	2.70	W	3.49	S
2.21	M	1.80	W	2.31	W	2.20	M
2.13	W	1.64	W	-	-	1.68	M

## 2. Preparation of New Dioxygenyl Salts - The Heat of Formation of $\text{O}_2^+\text{ClO}_4^-$

In our preceding quarterly report (Ref 1) we stated our intention to abandon efforts to synthesize new dioxygenyl salts because our attempts to carry out metathesis reactions with  $\text{O}_2\text{AsF}_6$  in anhydrous HF had resulted in the decomposition of the dioxygenyl cation. Since that time we have reconsidered our decision, reaching the conclusion that further efforts to prepare  $\text{O}_2^+$  salts of perchlorate, tetrafluorochlorate, nitrate, and  $\text{C}(\text{NO}_2)_3$  anions should be pursued in (a) different solvent media and (b) in the solid state. One reason for our decision is the result of a calculation of the heat of formation of the hypothetical salt,  $\text{O}_2^+\text{ClO}_4^-$ . The value obtained, +6.4 k.cal/mole, indicates a stability for  $\text{O}_2\text{ClO}_4$  comparable to that of  $\text{NO}_2\text{ClO}_4$  ( $\Delta H_f = +8.89$  k.cal/mole). The value for  $\text{O}_2\text{ClO}_4$  was calculated from equation 9 which relates the lattice

energy ( $U_{mx}$ ) of a salt to its heat of formation ( $H_{mx}$ ). The lattice energy is the internal energy change for the process shown in equation 10.

$$U_{mx} = H_{m+} + H_{x-} - (H_{mx} + 2RT) \quad (9)$$



In order to check the method of calculation, the lattice energy of  $\text{NaClO}_4$  at  $25^\circ\text{C}$  was calculated using the known thermodynamic values:

$$H_{\text{Na}^+}(g) = 146 \text{ k.cal/mole} \quad (\text{Ref 5})$$

$$H_{\text{ClO}_4^-}(g) = -80.5 \text{ k.cal/mole} \quad (\text{Ref 6})$$

$$H_{\text{NaClO}_4(s)} = -92.18 \text{ k.cal/mole} \quad (\text{Ref 5})$$

Substitution of these values into equation 9 ( $2RT = 1.2 \text{ k.cal/mole}$ ) yields  $U_{\text{NaClO}_4} = 156.5 \text{ k.cal/mole}$ . This result is in excellent agreement with a value of  $156.4 \text{ k.cal/mole}$  reported by Benito and Masia (Ref 7).

In order to calculate the heat of formation of  $\text{O}_2\text{ClO}_4$  from equation 9 it is necessary to know the lattice energy of  $\text{O}_2\text{ClO}_4$ . To estimate this the assumption is made that  $U_{\text{O}_2\text{ClO}_4} = U_{\text{NOClO}_4}$ . We have shown that  $\text{O}_2\text{AsF}_6$  and  $\text{NOAsF}_6$  are isomorphous (see Table III) so it is reasonable to expect the same to hold for the corresponding perchlorates. The lattice energy of  $\text{NOClO}_4$  can be calculated from the following data by insertion into equation 9:

$$H_{\text{NO}^+}(g) = H_{\text{NO}}(g) + I_{\text{NO}}(g) = 234.9 \text{ k.cal/mole}$$

$$H_{\text{NO}}(g) = +21.6 \text{ k.cal/mole} \quad (\text{Ref 5})$$

$$I_{\text{NO}}(g) = 213.3 \text{ k.cal/mole (Ionization Potential)} \quad (\text{Ref 8})$$

$$H_{\text{ClO}_4^-}(g) = -80.5 \text{ k.cal/mole}$$

$$H_{\text{NOClO}_4(s)} = -41.79 \text{ k.cal/mole} \quad (\text{Ref 9})$$

The lattice energy obtained for  $\text{NOClO}_4$  ( $U_{\text{NOClO}_4}$ ) is 195 k.cal/mole. The calculation of the heat of formation of  $\text{O}_2^+\text{ClO}_4^-$  is carried out as follows:

$$U_{\text{O}_2\text{ClO}_4} = U_{\text{NOClO}_4} = 195 \text{ k.cal/mole} = H_{\text{O}_2^+(g)} + H_{\text{ClO}_4^-(g)} - H_f_{\text{O}_2\text{ClO}_4} - 2RT \quad (11)$$

$$H_f_{\text{O}_2\text{ClO}_4}(s) = H_{\text{O}_2^+(g)} + H_{\text{ClO}_4^-(g)} - 2RT - 195 \quad (12)$$

$$H_{\text{O}_2^+(g)} = 283.1 \text{ k.cal/mole} \quad (\text{Ref 5}) \quad (13)$$

$$H_{\text{ClO}_4^-(g)} = -80.5 \text{ k.cal/mole} \quad (14)$$

$$H_f_{\text{O}_2\text{ClO}_4}(s) = 283.1 - 80.5 - 1.2 - 195 = +6.4 \text{ k.cal/mole} \quad (15)$$

In view of the fact that known compounds of chlorine and oxygen have heats of formation considerably less favorable than that estimated for  $\text{O}_2^+\text{ClO}_4^-$  ( $\text{ClO}_2 = +24.7$ ;  $\text{Cl}_2\text{O} = +18.2$ ,  $\text{Cl}_2\text{O}_7 = +63.4$ ) it appears that further efforts to synthesize a perchlorate of the dioxygenyl cation are definitely justified.

### III. EXPERIMENTAL

#### A. REACTIONS OF $O_2F_2$

##### 1. Reaction of $O_2F_2$ with Cesium Chloride

The initial reaction between CsCl and  $O_2F_2$ , experiment number 1, Table I, was carried out without any diluent medium. A 0.5736 gram sample of CsCl was treated with what visually appeared to be an excess of  $O_2F_2$  in a vacuum for 3 hours at  $-110^{\circ}C$ . The system was then warmed to  $-78^{\circ}C$  where it was maintained overnight. Some unreacted  $O_2F_2$  was still present the next day. The solid gave off white fumes as the mixture was allowed to warm up to room temperature. The white solid product weighed 0.6075 gram, which represented a 5.4% gain in weight. Although no chlorine-containing gases were recovered from the reaction, it is possible that some might have been discarded along with the  $O_2F_2$  decomposition products.

Considerable difficulty was encountered in getting the powdered product into a glass X-ray tube and when this was finally achieved, only the pattern of  $Cs_2SiF_6$  was seen. Results of chemical analysis of the product are shown in Table II. There was not enough material to get an infrared spectrum.

In experiment number 2, Table I, a relatively large amount of CsCl (2.4171 grams) was used. The reaction was carried out first at  $-107^{\circ}C$  for 3 hours and then at  $-78^{\circ}C$ . Ignition occurred between the reactants when the reactor was warmed to  $-78^{\circ}C$ . A rock-like yellow boule, weighing 2.4330 grams, was formed. Also  $ClO_2$ ,  $ClO_2F$ , and  $ClO_3F$  were identified in the gases formed during the reaction. Small amounts of impurities were detected too. These were:  $N_2O$ ,  $NO_2$ ,  $NOCl$ , and  $CO_2$ .

The solid product was found to be insensitive to impact and to give a rather weakly positive test for oxidizing power with acidic potassium iodide solution. The outer layer of the boule was yellow, whereas the inner portion was white, unreacted CsCl. The infrared spectrum of the product exhibited absorptions at 1235, 1520, 1835, and  $2050\text{ cm}^{-1}$ . The following correlations were made:  $1235\text{ cm}^{-1}$  ( $NO_2^-$ ),  $1520\text{ cm}^{-1}$  ( $NO_3^-$  or  $CO_3^{2-}$ ), and  $2050\text{ cm}^{-1}$  ( $N_3^-$  or  $C\equiv N^-$ ). However, chemical tests of the product for these ions were

negative with the possible exception of  $\text{CO}_3^-$ , the test for which was inconclusive. The product did not appear to react with KBr when it was pelletized for infrared analysis. A sample of the product was pyrolyzed at  $125^\circ\text{C}$  and  $350^\circ\text{C}$  in a vacuum and the resulting gases were analyzed by means of mass spectroscopy. Only  $\text{Br}_2$ , H Br, and fluorocarbons (from the Kel-F) reactor were detected. The bromine constituents were impurities picked up from the vacuum apparatus, which had been used previously for experiments with  $\text{BrF}_3$  and  $\text{BrF}_5$ . X-ray analysis of the residue of the pyrolysis identified it as  $\text{CsCl}$ .

Cesium chloride was also treated with  $\text{O}_2\text{F}_2$  in the presence of perfluoropropane diluent medium. The procedure described below used in experiments 3 and 4, Table I, was designed to drive the reaction, which was sluggish in  $\text{C}_3\text{F}_8$ , as nearly as possible to completion.

In experiment 3, Table I, a 1.6494 gram sample of  $\text{CsCl}$  was immersed in 6 cc of  $\text{C}_3\text{F}_8$ , to which  $\text{O}_2\text{F}_2$  was added. The mixture was allowed to stand one hour at  $-110^\circ\text{C}$  and then overnight at  $-78^\circ\text{C}$ . A yellow solid weighing 1.7514 grams was obtained, along with a significant amount of  $\text{ClO}_2$ . The solid was reground in the dry-box, and in experiment 4, 0.6257 grams of this was reloaded into the Kel-F reactor. To this was added  $\text{C}_3\text{F}_8$  and then over a period of several days freshly prepared batches of  $\text{O}_2\text{F}_2$  were added in an attempt to drive the reaction to completion. The yellow solid obtained as a result of this treatment weighed 0.6212 gram.

The solid gave a weakly positive test for oxidizing power with acidic potassium iodide solution. Although the product tended (as did all the others) to cake upon grinding, we were able to get a sample into a glass capillary tube. The X-ray pattern obtained was that of  $\text{Cs}_2\text{SiF}_6$ . Results of chemical analysis of the product from experiment number 4 are shown in Table II.

The procedure used in experiment 5, Table I, was designed to prevent the reactants from igniting when they were warmed to  $-78^\circ\text{C}$  in the absence of a solvent. A 0.626 gram sample of cesium chloride was pulverized to a powder and placed in a Kel-F reactor. Then it was treated with  $\text{O}_2\text{F}_2$  in a vacuum at  $-106^\circ\text{C}$ . The cold bath was allowed to warm from  $-106^\circ\text{C}$  to  $-95^\circ\text{C}$  over a period of 0.75 hours. When this temperature was reached a  $-78^\circ\text{C}$  bath was used and the reactor was kept at this temperature overnight. Succeeding batches of  $\text{O}_2\text{F}_2$  were made and allowed to react with the solid at  $-78^\circ\text{C}$  over a period of several days. This was done to insure that all of the cesium chloride would be converted to products. The resulting solid was gray before it was transferred to a dry-box for handling. There was also a small amount of a red solid on the walls of the

reactor which could not be recovered. No chlorine-containing gases were isolated from this particular reaction, although  $\text{ClO}_2$ ,  $\text{ClO}_2\text{F}$ , and  $\text{ClO}_3$  were obtained in similar ones.

After the solid was weighed (0.6383 gm), it was transferred to a dry-box. Although it had not been exposed to the air, it became yellow and moist in the dry-box. When it was poured through a glass funnel into a Kel-F bottle for storage, a white residue was formed on the glass, which was later shown by X-ray analysis to be  $\text{Cs}_2\text{SiF}_6$ . Almost immediately the solid in the Kel-F bottle turned to a yellow liquid. Some of this was put on infrared optics and analyzed in the open air. Water was found to be present; in view of this no further analytical work was performed on the product.

## 2. X-ray Analysis of $\text{CsF}$ - $\text{CsCl}$ Mixture

A 1:1 by weight mixture of  $\text{CsCl}$  and  $\text{CsF}$  was ground and mixed thoroughly. It was then placed in a capillary and analyzed by X-ray diffraction. The spectrum gave a very heavy pattern for  $\text{CsCl}$ , but only a couple of faint lines of  $\text{CsF}$  were seen. In contrast to the products obtained from  $\text{O}_2\text{F}_2$  and  $\text{CsCl}$  (which became moist upon grinding in the dry-box and formed  $\text{Cs}_2\text{SiF}_6$  with glass), the  $\text{CsCl}$ - $\text{CsF}$  mixture did not behave in this fashion. No  $\text{Cs}_2\text{SiF}_6$  was detected in the X-ray diffraction pattern of the mixture.

## 3. Attempted Reaction of $\text{O}_2\text{F}_2$ with $\text{CsClF}_4$

A 0.8210 gram sample of  $\text{CsClF}_4$  was treated with  $\text{O}_2\text{F}_2$  in a Kel-F reactor in a vacuum at  $-107^\circ\text{C}$  for 1.5 hours. Then the temperature was raised to  $-78^\circ\text{C}$  and held there overnight. The next day the salt was treated with fresh  $\text{O}_2\text{F}_2$  at  $-107^\circ\text{C}$  for 4 hours. The system was then kept at  $-78^\circ\text{C}$  for the succeeding two days. No change in the pink color of the salt was noted, nor were any volatile products obtained. The X-ray diffraction pattern of the solid residue failed to reveal the presence of any component other than  $\text{CsClF}_4$ .

## 4. Attempted Reaction of $\text{O}_2\text{F}_2$ with $\text{BrF}_5$ under Pressure

A micro-pressure reactor was constructed of Heliarc-welded 1/4 and 3/8 in. OD seamless, stainless steel tubing. This was fitted with an autoclave engineer's high-pressure valve. The reactor was closed off under vacuum and attached to a glass system used for generation of  $\text{O}_2\text{F}_2$ . The evacuated metal reactor was kept at  $-196^\circ\text{C}$  and the pressure valve at  $-78^\circ\text{C}$  while  $\text{O}_2\text{F}_2$  was condensed above the valve from the glass discharge system. However, attempts to gel the  $\text{O}_2\text{F}_2$  into the reactor were unsuccessful. Evidently it decomposed too rapidly at  $-78^\circ\text{C}$ ,

forming a backpressure in the region of the valve which prevented its drawing into the reactor. Thus the experiment had to be abandoned.

## B. REACTIONS OF TRIOXYGEN DIFLUORIDE

### 1. Reaction of $O_3F_2$ with $Cl_2$

One millimole of  $Cl_2$  was condensed at  $-196^{\circ}C$  into the bottom of a glass U-trap used for electrical discharge synthesis of  $O_3F_2$ . The temperature of the trap was maintained at  $-196^{\circ}C$  while the 3:2 molar ratio oxygen:fluorine mixture was electrolyzed in the low pressure arc to generate  $O_3F_2$ . Thus  $O_3F_2$  was deposited on the  $Cl_2$  at  $-196^{\circ}C$ . The top walls of the tube exhibited a narrow band of purple material after the  $O_3F_2$  had been formed. The temperature of the reactor was raised to  $-160^{\circ}C$  for 1.5 hours and a sample of the gases that were evolved was analyzed. Components identified by infrared spectroscopy were:  $COF_2$ ,  $NO_2Cl$ ,  $ClO_2F$ ,  $ClO_3F$ ,  $SiF_4$ , and  $ClO_2$ .

### 2. Reaction of $O_3F_2$ with $AsF_5$

The same procedure was used to evaluate the reaction of  $O_3F_2$  with  $AsF_5$  as was used for the reaction with  $Cl_2$ . The  $AsF_5$  and  $O_3F_2$  were allowed to stand in contact at  $-160^{\circ}C$  in a glass U-trap for 1.5 hours. The mixture was then allowed to warm to room temperature. The solid product that was recovered was  $O_2AsF_6$  which was identified by X-ray spectroscopy.

### 3. Reaction of $O_3F_2$ with NO

The same procedure was used as in the previously described reactions of  $O_3F_2$ . The mixture of  $O_3F_2$  and NO was allowed to stand in a glass U-trap at  $-196^{\circ}C$  for 3 hours, during which time there was no evidence of reaction. Then the temperature was raised to  $-185^{\circ}C$  for 2.5 hours. Infrared analysis of the gases from the reaction failed to reveal the presence of any volatile reaction products, and only trace impurities from the vacuum line were detected. The reactants were then allowed to stand at  $-78^{\circ}C$  overnight. The only two products identified after this treatment were  $NO_2$  and  $SiF_4$ .

### 4. Attempted Reaction of $O_3F_2$ with $NONF_2$

An attempt was made to carry out this reaction by condensing  $NONF_2$  onto  $O_3F_2$  at  $-196^{\circ}C$  in a quartz U-trap. The  $O_3F_2$  was generated electrolytically in the U-trap discharge tube and  $NONF_2$  was generated by passing  $N_2F_4$ -NO

mixture through a hot metal tube under vacuum conditions. During the course of the experiment, the side arm on the quartz U-trap was broken and the experiment was discontinued.

### 5. Attempted Reaction of $O_3F_2$ with $CsClF_4$

A sample of  $CsClF_4$  was loaded into a quartz U-trap used for electric discharge synthesis of  $O_3F_2$ . The trap was refrigerated at  $-196^{\circ}C$  and  $O_3F_2$  was generated. Then the trap was held at  $-107^{\circ}C$  for several hours and brought to  $-78^{\circ}C$  for a similar period. The only gases found to be present were  $C_2F_6$ ,  $CF_4$ , and  $SiF_4$ . X-ray diffraction analysis of the solid showed only the lines of the original  $CsClF_4$ .

## C. REACTIONS OF DIOXYGENYL SALTS

### 1. Reaction of $NF_2\cdot$ Radicals with $O_2AsF_6$

A metal, Kel-F system was used to evaluate this reaction. The  $N_2F_4$  was introduced slowly under vacuum conditions into a steel tube heated to  $250^{\circ}C$ . The  $NF_2\cdot$  radicals formed therein were passed into a Kel-F trap where they were condensed out at  $-196^{\circ}C$ . The trap contained 0.2098 gm of  $O_2AsF_6$ . The latter was kept at  $-196^{\circ}C$ . The level of the liquid nitrogen bath was such that the  $NF_2\cdot$  radicals were condensed directly onto the solid  $O_2AsF_6$ . As the  $NF_2\cdot$  radicals deposited on the walls of the tube near the  $O_2AsF_6$ , various colors—red, purple, and green were observed. No gases were given off at  $-196^{\circ}C$ . The mixture was then allowed to stand at  $-117^{\circ}C$ . The colors of the system thereupon changed to green and yellow. The reactor was then rechilled to  $-196^{\circ}C$  and the system was monitored by infrared and mass spectroscopy. No volatile materials were detected. The system was then allowed to warm up to room temperature. Mass spectrometric analysis showed that  $NF_3$  and  $O_2$ , along with trace amounts of  $NO_2$  and  $N_2$  were evolved. Results of infrared analysis of this same sample of gases are incomplete at this time.

The solid residue, which was white, was analyzed by X-ray diffraction. The pattern obtained was different from that of the original  $O_2AsF_6$ . It is compared in Table III to patterns of known hexafluoroarsenate-type compounds which could have been formed in the reaction. The pattern of the product does not match exactly that of any of the known compounds, although some  $O_2AsF_6$  (or  $NOAsF_6$ ) is obviously still present. When the product was stored in a Kel-F vial in a dry-box it began to volatilize; after five days only a small fraction of the original amount remained. Further analytical work on the small residue is in progress.

#### IV. FUTURE WORK

- The  $O_2F_2$ -CsCl reaction will be completely characterized.
- The solid product of the reaction of  $\cdot NF_2$  with  $O_2AsF_6$  will be analyzed.
- The reaction of  $O_2F_2$  with  $ClO\cdot AsF_5$  will be studied.
- The reaction of  $O_2AsF_6$  with  $NO_2ClO_4$  will be examined by DTA.
- The construction of an  $O_2F_2(O_3F_2)$  generator with infrared optics will be completed.

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**Section IV**

**Task 55**

**THERMAL STABILITY OF ADVANCED SOLID OXIDIZERS**

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Section IV

**THERMAL STABILITY OF ADVANCED SOLID OXIDIZERS**

C. J. Grelecki

W. Cruice

Report RMD 5043-Q3-64

RMD Project 5043, Task 55  
Report Period: 1 July 1964 to  
30 September 1964

Contract No. NOnr 4364(00)  
ARPA Order No. 417  
Project Code 4910

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**FOREWORD**

This section of the advanced oxidizer report summarizes work carried out during the period from 1 July 1964 to 30 September 1964 on the thermal stability of advanced solid oxidizers (RMD Project 5043, Task 55).

Contributors to the research were: C. Grelecki (Project Supervisor) and W. Cruice (Principal Investigator).

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CONTENTS

	Page
I. INTRODUCTION	1
II. SUMMARY	2
III. EXPERIMENTAL	3
A. Procedures	3
B. Materials	3
IV. RESULTS AND DISCUSSION	4
A. Thermal Decomposition of Hydrazinium Perchlorate — Kinetics	4
B. Thermal Decomposition of Hydrazinium Perchlorate — Stoichiometry and Mechanism	6
V. FUTURE WORK	9
VI. REFERENCES	10

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Task 55  
Report RMD 5043-Q3-64

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**ILLUSTRATIONS**

<b>Figure</b>		<b>Page</b>
1	Thermal Decomposition of HP at Various Temperatures	5
2	Selected Values of Kinetic Constant C Versus $\frac{1}{T (^\circ K)}$	7

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## 1. INTRODUCTION

The objective of this program is to study the kinetics of the thermal reactions of high energy oxidizers in order to understand the mechanism by which they decompose. Work previously reported included highlights of a preliminary literature search, results of experimental work on the vapor pressure and thermal decomposition of anhydrous  $\text{HClO}_4$ , and results of initial experiments on the thermal decomposition of high purity HP (hydrazinium perchlorate).

Work on the thermal decomposition of high purity HP has been extended to cover the entire range from  $140^{\circ}\text{C}$  to  $200^{\circ}\text{C}$ . Elementary kinetic equations have been formulated and kinetic constants have been evaluated. Preliminary studies on the stoichiometry and mechanism have been performed and a sound basis has been prepared for more extensive and exacting experiments on the decomposition path. The preparation of hydroxylammonium perchlorate (HAP) has been studied and samples of this material have been prepared and given preliminary shock tests. Other solid aminoperchlorate oxidizers are being prepared and purified for experimentation.

This report includes a summary of experimental work done in the third quarter and a brief summary of projected experiments for the following quarter.

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## II. SUMMARY

During this report period thermal decomposition studies on hydrazinium perchlorate were performed through the range 140° to 200°C.

The rate of evolution of gaseous products was converted to moles of gas per mole of HP initially present ( $n/N_0$ ) and was found to follow two different equations at different parts of the experiment. During the early part of the reaction the expression  $n/N_0 = At^2+B$  describes the curve; during the middle part of the reaction, the rate is constant according to  $n/N_0 = C(t-D)$ ; and when  $n/N_0 > 0.600$ , the rate decreases in an irregular manner due to freezing out of solid products. The values of A, B, C and D have been determined as a function of temperature.

The stoichiometry,  $8N_2H_5ClO_4 \longrightarrow 7NH_4ClO_4 + NH_4Cl + 4N_2 + 4H_2O$ , has been proposed and the presence of considerable  $NH_4^+$  and some  $Cl^-$  in the residues of decomposition runs has been established. The ratio of non-condensable gases to condensable gases at room temperature at the end of the decomposition runs is 1.00 as would be expected since the predicted proportion of  $N_2$  to  $H_2O$  is 1.00. Non-condensable gaseous products have been identified as primarily (97+ %)  $N_2$  by mass spectrographic analysis. The mechanism is visualized as beginning with the dissociation of HP to  $N_2H_4$  and  $HClO_4$ , followed by the oxidation of  $N_2H_4$  to  $NH_3$  and water by  $HClO_4$  and by the semi-stable oxides of chlorine.

Efforts to prepare HAP in purity satisfactory for kinetic studies have met with little success thus far. Modifications of the method patented by Robson (previously referenced) are being tested in hopes of producing purer material.

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### III. EXPERIMENTAL

#### A. PROCEDURES

The methods used in our experiments have been discussed in detail in the previous quarterly reports.

#### B. MATERIALS

##### 1. Hydrazinium Perchlorate (HP)

All HP used in thermal decomposition experiments is produced in the manner previously reported with the same high purity standards applied to each batch before use.

##### 2. Hydroxylammonium Perchlorate (HAP)

Synthesis of HAP by the method of Robson previously discussed have not been successful in producing material of satisfactory purity for use in thermal decomposition experiments. All attempts made to date to remove occluded solvent present in the final product have resulted in some degradation and discoloration. Modifications of Robson's method are being evaluated in hopes of producing higher purity HAP than has been available thus far.

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REACTION MOTORS DIVISION**IV. RESULTS AND DISCUSSION****A. THERMAL DECOMPOSITION OF HYDRAZINIUM PERCHLORATE — KINETICS**

Thermal decomposition experiments on high-purity HP have been performed in the apparatus previously described through the temperature range 140° to 200°C. For convenience in comparing results of different runs, P vs t data are converted to  $n/N_0$  vs t, where n = moles of gaseous products (by  $PV = nRT$ ) and  $N_0$  = initial amount of HP present (as moles). In all experiments the initial portion of the  $n/N_0$  vs t curve follows the expression  $n/N_0 = At^2 + B$ ; this equation is succeeded by a linear relationship,  $n/N_0 = C(t-D)$ , which characterizes the main portion of the curve. At high values of  $n/N_0$  ( $> 0.600$ ), the linear law fails as products normally solid at these temperatures begin to freeze out and a decline in rate is observed. Results of runs at various temperatures are presented graphically in Figure 1; the constants A, B, C and D are tabulated below, as well as values of  $t_i$  (time of initial period) and  $n/N_0$  at  $t_i$ .

TABLE I  
THERMAL DECOMPOSITION PARAMETERS FOR HP

Temp (°C)	<u>A x 10<sup>8</sup></u>	<u>B</u>	<u>C x 10<sup>4</sup></u>	<u>D</u>	<u><math>t_i</math>*</u>	<u><math>n/N_0</math> at <math>t_i</math>*</u>
140	6.25	0	1.31	552	1200	0.090
150	22.9	0	3.25	320	480	0.080
158	107	-0.006	6.9	166	300	0.090
170	260	-0.020	10.9	104	170	0.070
181	1070	0	21.0	53	95	0.090
200	18,000	+0.020	86.0	10	27	0.140

\*Approximate values - time in minutes

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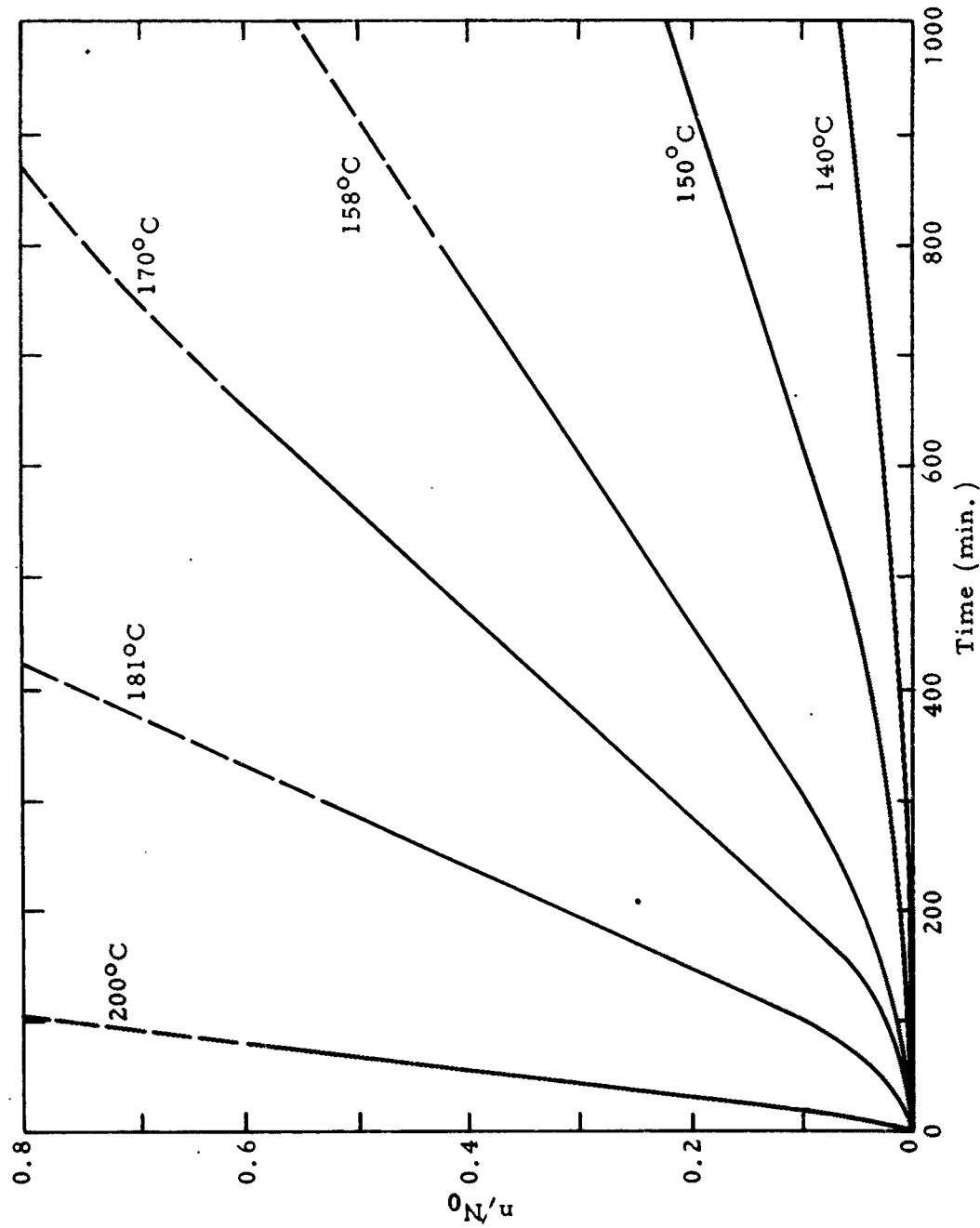


Figure 1. Thermal Decomposition of HP at Various Temperatures

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The values reported here at 150° C replace the values previously reported (Report RMD 5043-Q2-64) which were found to be in error; the reaction proceeds more rapidly at 150° C than at 140° C, as might have been expected. It is of interest to note that the decomposition follows the power law when the HP is molten as well as when it is solid. The power law dependence is expected when the decomposing material is solid, as in the process "Nucleation According to a Power Law - Normal Growth", so frequently found to apply (Ref 1). However, no such theory has been advanced to predict such dependence when the decomposing material is molten and there are no active centers or decomposition nuclei.

1

A plot of various values of  $\log "C"$  versus  $\frac{1}{T(\text{°K})}$  (reproduced in Figure 2) shows some scatter; the overall activation energy for the linear portion of the  $n/N_0$  vs  $t$  curve calculated from this Arrhenius plot is 23.8 kcal/mole.

#### B. THERMAL DECOMPOSITION OF HYDRAZINIUM PERCHLORATE — STOICHIOMETRY AND MECHANISM

Residual pressures taken at room temperature some time after the sickle gage has been removed from the high temperature bath are converted to moles for comparison with the final reading at elevated temperature. At lower temperatures (140° to 158° C), the molar ratio of non-condensable gases to condensable gases is characteristically unity (within experimental error after  $PV = nRT$  calculations). At higher temperatures this ratio decreases to 0.85 at 181° C and 0.79 at 190° C. This decrease in the molar ratio of non-condensables to condensables is supposedly caused by the vapor pressures of HP and of other reaction products of negligible vapor pressures at the lower temperatures. It is also possible that the reaction path may be different at higher temperatures, i.e., that active intermediates may decompose to form different products when the temperature is higher.

Analysis of solid residues showed only  $\text{NH}_4^+$  and  $\text{Cl}^-$  in addition to  $\text{N}_2\text{H}_4$  and  $\text{ClO}_4^-$ . Due to the size of the samples involved (initial mass of HP = 0.100 gm) it has not been possible to obtain satisfactory quantitative data. Non-condensable gases were analyzed by mass spectrograph repeatedly with virtually identical results — 95+%  $\text{N}_2$  and traces of  $\text{H}_2$ . (The hydrogen fraction was usually of the order of 1% or less). On the basis of work reported in the literature on  $\text{N}_2\text{H}_5\text{Cl}$ ,  $\text{N}_2\text{H}_5\text{NO}_3$ , and other salts of hydrazine (Ref 2), the stoichiometry,  $8\text{N}_2\text{H}_5\text{ClO}_4 \longrightarrow 7\text{NH}_4\text{ClO}_4 + \text{NH}_4\text{Cl} + 4\text{N}_2 + 4\text{H}_2\text{O}$ , was proposed.

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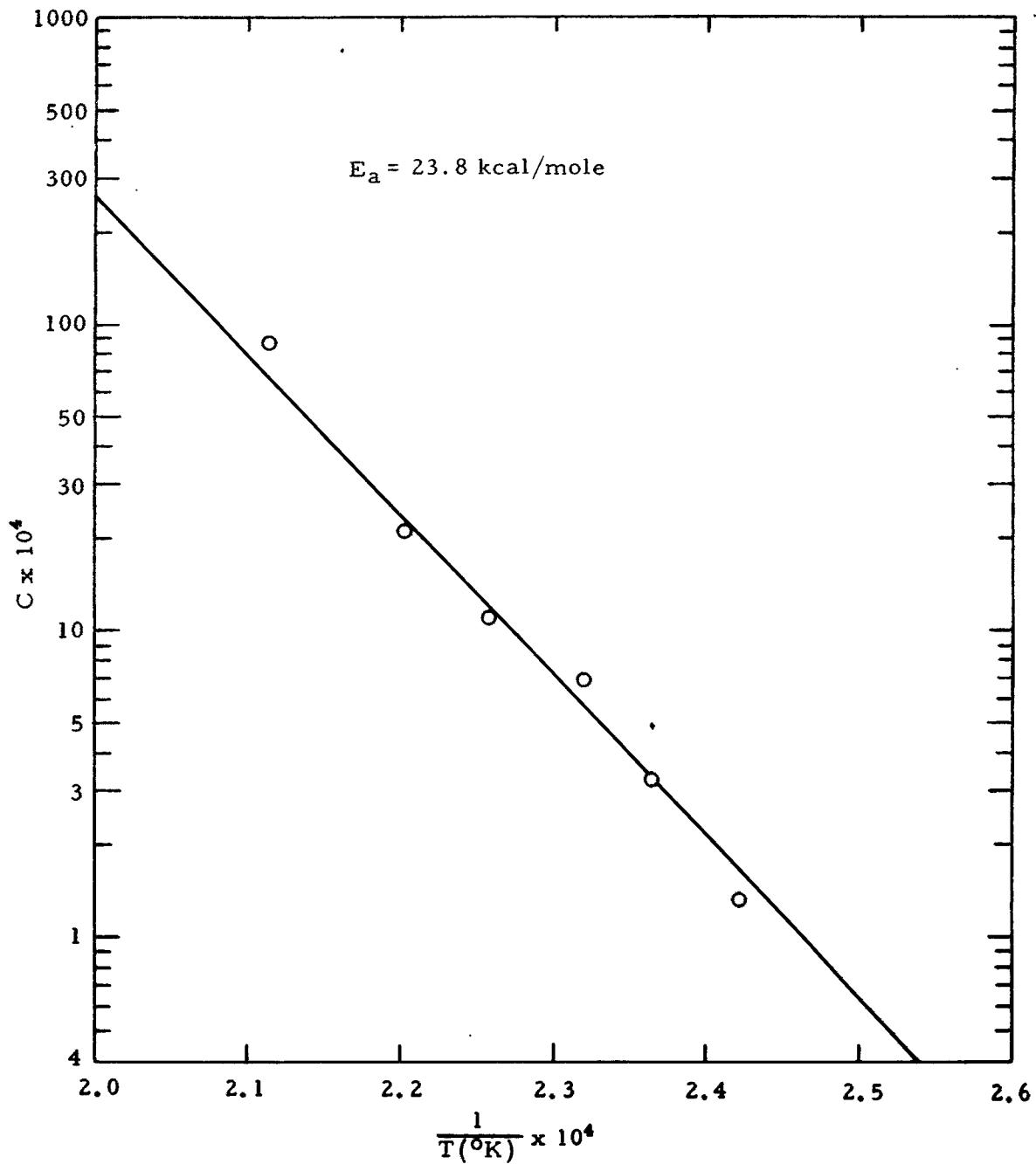


Figure 2. Selected Value of Kinetic Constant C versus  $\frac{1}{T} \times 10^4$

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The proposed stoichiometry is consistent with the following reaction sequence.

The initial step is presumably a proton transfer which results in dissociation as follows:

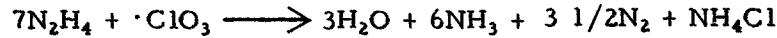


Such a proton transfer has also been suggested as the initial step in the decomposition of  $\text{NH}_4\text{ClO}_4$ .

Perchloric acid is unstable at the temperature of the reaction and decomposes to active oxidizing radicals. The initial dissociation which is thermodynamically favored is:



Other oxidizing intermediates are also possible and they, in conjunction with the ones shown above, oxidize hydrazine as follows:



Thus, eight hydrazine units are oxidized per perchlorate unit lost. The overall expression includes all of the products found and also is consistent with the observed ratio of non-condensable to condensable gases. However, further experiments on the stoichiometry of this reaction are required to definitely determine the reaction path.

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## V. FUTURE WORK

During the next period primary effort will be devoted to the preparation of HAP of satisfactory purity for accurate kinetic experiments, and the performance of an exploratory study of the vapor pressure and thermal decomposition characteristics of this compound. Extensive efforts will be made to establish the activation energy, stoichiometry and mechanism of the thermal decomposition reaction and, wherever possible, comparisons will be made between HAP, HP, and other oxidizers for which appropriate information is available.

Additional work on anhydrous  $\text{HClO}_4$  is also scheduled. Extension of vapor pressure studies to higher temperatures and confirmation of pressures already reported are important to the overall purpose of the program.

Specific experiments planned for the future include:

- Completion of survey of thermal decomposition of HP
- Determination of vapor pressures of HAP
- Determination of thermal decomposition characteristics of HAP
- Extension of vapor pressure measurements on anhydrous  $\text{HClO}_4$  to higher temperatures
- Confirmation of vapor pressures of anhydrous  $\text{HClO}_4$  previously reported.

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**Section V**

**Tasks 56 and 54**

**CHEMISTRY OF DIFLUORODIAZINE AND NITROSYL FLUORIDE  
AND  
STABILIZATION OF NITRONIUM PERCHLORATE**



## Section V

### Tasks 56 and 54

### CHEMISTRY OF DIFLUORODIAZINE AND NITROSYL FLUORIDE AND STABILIZATION OF NITRONIUM PERCHLORATE

A. R. Young  
D. Moy  
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Report RMD 5043- Q3-64

RMD Project 5043, Tasks 56 and 54  
Report Period: 1 July 1964 to  
30 September 1964

Contract No. NOnr 4364(00)  
ARPA Order No. 417  
Project Code 4910

## FOREWORD

This section of the Advanced Oxidizer Research report summarizes results obtained in our study of the "Chemistry of Difluorodiazine and Nitrosyl Fluoride" (Task 56) during the period from 1 July 1964 to 30 September 1964, as well as previously unreported results on "The Stabilization of Nitronium Perchlorate by Complexation" (Task 54). Work in the area of nitronium perchlorate stabilization was terminated during this quarter and personnel previously assigned to that task have transferred their efforts to the study of difluorodiazine chemistry.

Contributors to the work reported in this section were: A. R. Young, (Project Supervisor), D. Moy, J. Dvorak, J. Crothamel, D. Kates, R. Caruso, and B. Fagan.

CONTENTS

	Page
I. INTRODUCTION	1
II. DISCUSSION	2
A. Reactions of $N_2FAsF_6$	2
B. Reactions of <u>cis</u> - $N_2F_2$	5
C. Preparation of Difluorodiazine	7
D. Reaction Between $N_2F_4$ and $AsF_5$	8
E. Attempted Preparation of New Perchlorate Oxidizers	9
III. EXPERIMENTAL	13
A. Reactions of $N_2FAsF_6$	13
B. Reactions of <u>cis</u> - $N_2F_2$	14
C. Preparation of <u>trans</u> - $N_2F_2$	15
D. Attempts to Prepare New Perchlorates	16
IV. FUTURE WORK	18
V. REFERENCES	19

TABLES

	Page
I. X-Ray Diffraction Pattern of $\text{NOF} \cdot 3\text{HF} \cdot \text{cis-N}_2\text{F}_2$ Reaction Product	7
II. X-Ray Diffraction Pattern of Residue from $\text{NO}_2 \text{ClO}_4$ - $\text{HClO}_4$ Solution	10
III. Analysis of $\text{NO}_2\text{ClO}_4$ - $\text{HClO}_4$ Reaction Product	10
IV. Analysis of $\text{NH}_3\text{OHCLO}_4$	11

## I. INTRODUCTION

This research program is concerned with the chemistry of difluorodiazine and nitrosyl fluoride, the ultimate objective being to prepare N-F solid oxidizers from these reagents.

In the previous report (Ref 1) a description was given of the characterization of the reaction product of cis-difluorodiazine with arsenic pentafluoride as an inorganic diazonium salt,  $\text{N}_2\text{F}^+$  $\text{AsF}_6^-$ . During the past quarter, attempts were made to prepare other  $\text{N}_2\text{F}^+$  derivatives by direct reactions of cis-difluorodiazine with potential fluoride ion acceptors, and by metathesis reactions of  $\text{N}_2\text{FAsF}_6$ . In some of the attempted reactions inconclusive results were obtained and further studies must be made in order to determine whether the synthesis of an energetic  $\text{N}_2\text{F}^+$  derivative is feasible.

Our supply of cis-difluorodiazine was depleted during this quarter and some effort was devoted to the synthesis of difluorodiazine from tetrafluorohydrazine. We were able to prepare a small quantity of the trans-isomer by a reaction of a previously unreported solid  $\text{N}_2\text{F}_4\text{-AsF}_5$  adduct with nitric oxide, but the yield of trans- $\text{N}_2\text{F}_2$  attainable by this method decreases as the scale of the reaction is increased. Quite recently 100-150 grams of  $\text{N}_2\text{F}_2$  (cis-trans mixture) was ordered from the Ozark-Mahoning Company.

Some results obtained in studies of the  $\text{NO}_2\text{ClO}_4\text{-HClO}_4$  system and of the action of perchloryl fluoride on hydroxylamine perchlorate are included in this report. Efforts in the area of nitronium perchlorate stabilization which were conducted under Task 54 have been terminated; we feel that our results show that the stabilization of nitronium perchlorate by complex formation is not feasible.

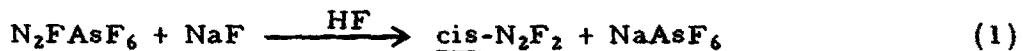
## II. DISCUSSION

### A. REACTIONS OF $N_2FAsF_6$

The preparation and characterization of fluorodiazonium hexafluoroarsenate was described in the preceding quarterly report (Ref 1). The adduct was shown to be a true ionic salt containing the energetic fluorodiazonium cation. The principal goal in continuing the study of the reaction of this salt is the coupling of the fluorodiazonium cation with suitable energetic anions to form potentially useful solid oxidizers.

#### 1. Reactions of $N_2FAsF_6$ in Anhydrous Hydrogen Fluoride

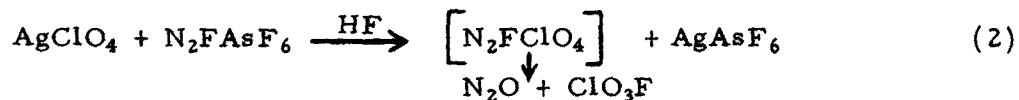
The high solubility at room temperature of the fluorodiazonium salt in anhydrous hydrogen fluoride indicated the feasibility of using HF as a reaction medium for metathesis reactions. This was borne out by the results of a test reaction (equation 1) in which cis-difluorodiazine was liberated quantitatively



from a mixture of fluorodiazonium hexafluoroarsenate and sodium fluoride in anhydrous HF. However, the use of HF as a medium for metathesis has the disadvantage that few anions other than fluoride can exist in this solvent.

(a) Reaction with  $AgClO_4$  and  $NH_4SO_3F$  - When solutions of fluorodiazonium hexafluoroarsenate in anhydrous HF were mixed with slurries of silver perchlorate or ammonium fluosulfonate in anhydrous HF at room temperature, instantaneous reactions occurred as evidenced by the rapid evolution of gaseous products. Solid phases were left suspended in HF and presumed to be silver hexafluoroarsenate-silver perchlorate and ammonium hexafluoroarsenate-ammonium fluosulfonate mixtures, respectively (no N-F materials were present). The gaseous fraction in each experiment was distilled out of the reaction tube and consisted of completely condensable gases at  $-196^{\circ}C$ . In the silver perchlorate reaction, the gaseous fraction contained approximately equivalent amounts of nitrous oxide and perchloryl fluoride. In the ammonium fluosulfonate reaction, the gaseous products were observed to be nitrous oxide and sulfuryl fluoride, again in roughly equivalent amounts.

The gaseous products from the two reactions can be readily accounted for by assuming the initial formation of fluorodiazonium perchlorate and fluosulfonate, respectively (equations 2 and 3), followed immediately by decomposition of the salts in HF at room temperature.

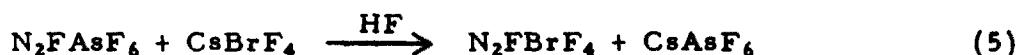


The failure to isolate fluorodiazonium perchlorate and fluorodiazonium fluosulfonate in these experiments does not necessarily preclude the possibility that these compounds are isolable by metathesis in solution. Several variables must be investigated before making a final judgment, namely:

- The effect of concentration on the rate of decomposition (rate of  $\text{N}_2\text{O}$  formation)
- The effect of temperature on the rate of decomposition
- The nature of the solvent.

In addition, the possibility must be examined that although  $\text{N}_2\text{F}^+$  and  $\text{ClO}_4^-$  or  $\text{SO}_3\text{F}^-$  ions react vigorously in the dissolved state, they may be stabilized in an ionic lattice.

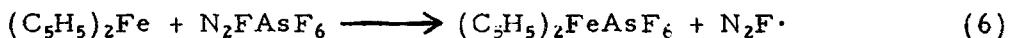
(b) Reactions with  $\text{ClF}_4^-$  and  $\text{BrF}_4^-$  Salts - Synthesis of fluorodiazonium tetrafluorochlorate or hexafluorobromate might be achieved by metathesis reactions in HF since all the ionic species involved are fully fluorinated and stable in HF (equations 4 and 5).



Identical behavior was observed when  $N_2FAsF_6$  solutions in HF were added to slurries of  $CsClF_4$  and  $CsBrF_4$ , respectively, in HF. There was only a slight amount of gas evolution ( $N_2O$ , cis- $N_2F_2$ ). The HF and insolubles were separated by decantation. Upon evaporation of the HF, only a trace amount of solid residue was observed. The insoluble fraction in each case was a gummy solid that could not be completely dried by pumping at room temperature.

Attempts to obtain infrared spectra of the solids as mulls were not successful because of reactions with the mulling agent (Kel-F oil). The surface characteristics of the solids (moist, gummy) made it almost impossible to prepare samples for X-ray analysis, but a weak powder pattern was obtained with the  $CsClF_4$  product. It shows several lines attributable to  $CsAsF_6$ , one of the products of the proposed metathesis (equation 4). There were lines present which could not be assigned to  $CsAsF_6$ , lending some hope that the desired  $N_2FClF_4$  had been synthesized. It will be interesting to examine the DTA curves of solid mixtures of  $CsClF_4$  and  $N_2FAsF_6$  for indications of metathesis in the solid state.

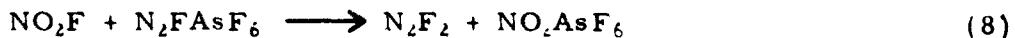
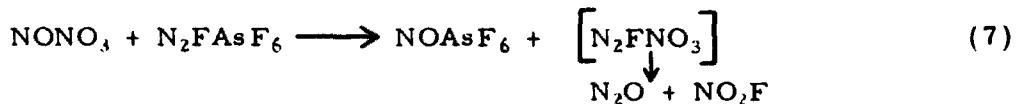
(c) Reaction of Ferrocene with  $N_2FAsF_6$  - The reaction of ferrocene with  $N_2FAsF_6$  is currently being investigated as a possible system for generating free radicals for coupling reactions (equation 6).



In a preliminary experiment the two solids were mixed in a Kel-F tube and they deflagrated instantly. The reaction of  $N_2FAsF_6$  with ferrocene in liquid HF will be explored in an attempt to produce the desired result.

## 2. Reaction of $N_2FAsF_6$ with $N_2O_4$

The reaction of  $N_2FAsF_6$  with liquid  $N_2O_4$  gave results similar to those obtained with  $AgClO_4$  and  $NH_4SO_3F$  in anhydrous hydrogen fluoride. At the melting point of  $N_2O_4$  (-9°C) a vigorous reaction took place, the products of which were  $N_2O$ , cis- $N_2F_2$ ,  $NO_2F$  (trace),  $NOAsF_6$  and  $NO_2AsF_6$ . These products might have arisen as shown in equations 7 and 8.



3. Reactions of  $\text{ClF}_3$  and  $\text{BrF}_5$  with  $\text{N}_2\text{FAsF}_6$

Chlorine trifluoride and bromine pentafluoride were examined as possible solvents for fluorodiazonium hexafluoroarsenate. However, in each case, the fluorodiazonium ion reacted to give cis-difluorodiazine and a solid residue, presumably  $\text{ClF}_2\text{AsF}_6$  and  $\text{BrF}_4\text{AsF}_6$ .

B. REACTIONS OF cis- $\text{N}_2\text{F}_2$

The reaction between cis-difluorodiazine and arsenic pentafluoride proceeds well in the gas phase at room temperature or below. It was thought, therefore, that other fluorodiazonium salts could be prepared by reacting cis-difluorodiazine with likely fluoride acceptors under moderate conditions.

1. Attempted Reaction of cis- $\text{N}_2\text{F}_2$  with  $\text{BiF}_5$

Since several stable  $\text{BiF}_6^-$  salts have been reported (Ref 2), the action of  $\text{N}_2\text{F}_2$  on bismuth pentafluoride was studied. However, no reaction was observed between bismuth pentafluoride and cis-difluorodiazine either at room temperature or at elevated temperatures. Addition of anhydrous HF to the system did not change the results. In a separate experiment, a solution of the fluorodiazonium hexafluoroarsenate in HF was mixed with a slurry of bismuth pentafluoride in HF, again with no sign of reaction.

2. Attempted Reaction of  $\text{PF}_5$  with cis- $\text{N}_2\text{F}_2$

Attempts were made to form fluorodiazonium hexafluorophosphate on the silver chloride window of a low temperature IR cell by condensing phosphorus pentafluoride and cis-difluorodiazine onto the window. No evidence for the formation of the desired product was found. A recent report (Ref 8) indicates that  $\text{N}_2\text{F}^+\text{PF}_6^-$  can be synthesized under high pressure conditions.

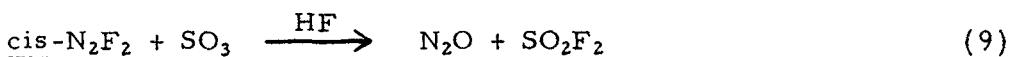
3. Attempted Reactions of  $\text{ClF}_3$ ,  $\text{BrF}_3$ , and  $\text{BrF}_5$  with cis- $\text{N}_2\text{F}_2$

Attempts were made to form the fluorodiazonium salts of the complex interhalogen fluorides by reacting the interhalogen compound with cis-difluorodiazine. With bromine trifluoride, decomposition of difluorodiazine was observed with the resulting oxidation of bromine trifluoride to the pentafluoride. In the cases of chlorine trifluoride and bromine pentafluoride, the only observable reaction was the slow thermal decomposition of difluorodiazine. The decomposition was accelerated at higher temperatures.

4. Attempted Reaction of  $\text{N}_2\text{F}_2$  with  $\text{SO}_3$ ,  $\text{SF}_4$ , and  $\text{SnF}_4$

Solid stannic fluoride did not react with cis-difluorodiazine at temperatures up to  $150^\circ\text{C}$ . Only thermal decomposition of difluorodiazine was observed.

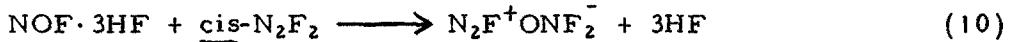
With gaseous sulfur trioxide, a reaction occurred at elevated temperature to give a mixture of noncondensable (at  $196^\circ\text{C}$ ) gases, nitrous oxide, and traces of a gaseous sulfur-fluorine compound. Addition of anhydrous HF accelerated the reaction and substantial quantities of nitrous oxide and sulfonyl fluoride were observed (equation 9). The reaction probably proceeded through the formation of the fluosulfonic acid.



Sulfur tetrafluoride and cis-difluorodiazine appeared to react to some extent to produce a small amount of white solid accompanied by a decrease in the amount of cis-difluorodiazine.

5. Attempted Reaction of  $\text{NOF} \cdot 3\text{HF}$  with cis- $\text{N}_2\text{F}_2$

The reaction of cis- $\text{N}_2\text{F}_2$  with  $\text{NOF} \cdot 3\text{HF}$  is currently being investigated as a route to new inorganic N-F compounds (equation 10).



In a preliminary experiment conducted in an NMR tube, the broad HF type peak observed for  $\text{NOF} \cdot 3\text{HF}$  at  $175 \pm 10$  ppm upfield from  $\text{CFCl}_3$ , shifted upon introduction of cis- $\text{N}_2\text{F}_2$  to  $187 \pm 6$  ppm upfield from  $\text{CFCl}_3$ . This observation suggests that the fluorine exchange in the complex,  $\text{NOF} \cdot 3\text{HF}$ , was reduced after the introduction of cis- $\text{N}_2\text{F}_2$ . After pumping on the reaction mixture a small amount of a white solid was obtained which had an X-ray powder pattern not previously encountered (Table I). A hydrolysate of the solid product oxidized KI and gave a positive test for  $\text{NO}_2^-$ .

The reaction was repeated on a larger scale in order to obtain a sufficient amount of solid for analysis. Excess cis- $\text{N}_2\text{F}_2$  was condensed on  $\text{NOF} \cdot 3\text{HF}$  at  $-196^\circ\text{C}$  and the reaction mixture was allowed to warm slowly to room temperature. After stirring overnight the gaseous fraction was found to contain cis and trans- $\text{N}_2\text{F}_2$  and  $\text{N}_2\text{O}$ . The solid product was isolated by pumping on the liquid

fraction. The infrared spectrum of this solid shows an absorption at  $2315\text{ cm}^{-1}$  attributable to  $\text{NO}^+$ , and a broad absorption band at  $640\text{ cm}^{-1}$  with a shoulder at  $720\text{ cm}^{-1}$ . Mass spectroscopic analysis of the solid reaction product is pending.

TABLE I  
X-RAY DIFFRACTION PATTERN OF  $\text{NOF} \cdot 3\text{HF}$ -  
cis- $\text{N}_2\text{F}_2$  REACTION PRODUCT

<u>d</u>	<u><math>I/I_0</math></u>
5.91	100
4.79	2
3.66	2
3.32	5
3.11	10
2.751	25
2.637	10
2.560	1
2.292	40
2.085	20
1.828	15
1.746	3
1.637	4
1.495	4
1.493	3
1.433	1
1.374	5

### C. PREPARATION OF DIFLUORODIAZINE

For some time difluorodiazine has not been available commercially. Since our laboratory supply was expended, it was necessary to undertake the synthesis of this compound. Commercial large scale preparations of difluorodiazine are normally accomplished through the fluorination of hydrazoic acid (Ref 3) or the electrolysis of molten ammonium bifluoride (Ref 4). Both methods yield a mixture of the cis and trans isomers, but the principal products are other fluorides of nitrogen. Because of the hazardous nature of the fluorination reaction and the

specialized equipment necessary for the electrolytic method, neither process was used. Instead, two methods of synthesizing difluorodiazine from tetrafluorohydrazine were tested.

1. Reaction of  $\text{AlCl}_3$  and  $\text{N}_2\text{F}_4$

The reaction of aluminum chloride with tetrafluorohydrazine is reported (Ref 5) to yield up to 40% difluorodiazine. We found that the reaction conditions must be controlled very carefully in order to achieve upwards of 40% yields. In particular, if the starting pressure of tetrafluorohydrazine is very high (as is necessary in preparing moderate amounts of difluorodiazine), the yield of difluorodiazine is decreased drastically with an accompanying increased yield of nitrogen trifluoride. For this reason, this method was not pursued further.

2. Reaction of  $\text{N}_2\text{F}_4 \cdot x\text{AsF}_5$  with NO

A moderately stable adduct is formed by reacting tetrafluorohydrazine with excess arsenic pentafluoride. trans-Difluorodiazine can be generated from this adduct in up to 50% yield by reaction with nitric oxide at room temperature. Because of the consistently high yields, and apparent insensitivity of the yield to small changes in reaction condition, this method was used to prepare quantities of trans-difluorodiazine up to 1 gram. The trans-difluorodiazine was purified by gas chromatography using a 10 ft molecular sieve 13X column.

D. REACTION BETWEEN  $\text{N}_2\text{F}_4$  AND  $\text{AsF}_5$

The stoichiometry and structure of the adduct formed between tetrafluorohydrazine and arsenic pentafluoride has not been determined. The formation of the solid proceeds well at room temperature by reacting gaseous tetrafluorohydrazine and excess arsenic pentafluoride at moderately high pressures (approximately 2-3 atm. total pressure). By simply measuring the amounts of unreacted gases recovered after formation of the adduct, we have not yet been able to fix the stoichiometry. With more precise measurements and more carefully controlled reaction conditions, it is hoped that the stoichiometry can be determined.

The adduct is thermally unstable at room temperature giving off both nitrogen trifluoride and trans-difluorodiazine. Arsenic pentafluoride was not detected as a product of the thermal decomposition at room temperature. Thus, the solid may change composition on standing.

An X-ray diffraction pattern was obtained after the adduct had remained at room temperature for several days. It was almost identical to diffraction patterns

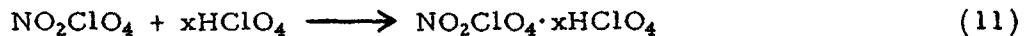
of nitrosyl and nitroso  $\text{Li}_3\text{Al}_2\text{F}_6$  hexafluoroarsenates (cubic,  $a = 8.00 \text{ \AA}$ ). The implication of this result is that the original solid adduct or the product of its thermal decomposition is ionic. An infrared analysis of the freshly prepared adduct showed the hexafluoroarsenate ion. However, the solid appeared to react to some extent with the mulling agent. On hydrolysis of the adduct, oxides of nitrogen and trans-difluorodiazine were evolved.

#### E. ATTEMPTED PREPARATION OF NEW PERCHLORATE OXIDIZERS

This section of the report is a discussion of the results of the final experiments performed on Task 54 of this program (Stabilization of Nitronium Perchlorate). Attempts were made to form  $\text{HClO}_4$  addition complexes of  $\text{NO}_2\text{ClO}_4$  and  $\text{HONH}_3\text{ClO}_4$ , respectively. Both salts were very soluble in anhydrous perchloric acid, but no evidence of stable complex formation was obtained. An attempt to prepare  $\text{NH}_3\text{ClO}_4^+\text{ClO}_4^-$  by the action of  $\text{ClO}_3\text{F}$  on  $\text{HONH}_3\text{ClO}_4$  was also unsuccessful.

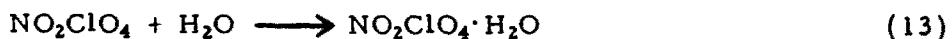
##### 1. Attempted Reaction of $\text{NO}_2\text{ClO}_4$ with $\text{HClO}_4$

The reaction of  $\text{NO}_2\text{ClO}_4$  with anhydrous  $\text{HClO}_4$  was explored as a possible route to a stable complex perchlorate (equation 11). Anhydrous perchloric acid



was condensed on  $\text{NO}_2\text{ClO}_4$  at  $-196^\circ\text{C}$  and the mixture was then allowed to warm to room temperature. After stirring the resultant solution for several hours, the  $\text{HClO}_4$  was removed in vacuo. The residual white solid had an X-ray powder pattern (Table II) unlike that of the original  $\text{NO}_2\text{ClO}_4$ . The infrared spectrum of the reaction product obtained as a mull showed absorptions attributable to  $\text{OH}$ ,  $\text{NO}_2^+$  and  $\text{ClO}_4^-$ . Chemical analysis, however, was in excellent agreement with theory for pure  $\text{NO}_2\text{ClO}_4$  (Table III).

It is possible that a monohydrate of  $\text{NO}_2\text{ClO}_4$  was formed through a sequence of reactions such as (equations 12 and 13). However, a chemical analysis indicates



the reaction product is predominantly  $\text{NO}_2\text{ClO}_4$ , and the observed X-ray diagram may be due to a modification of the crystal structure of  $\text{NO}_2\text{ClO}_4$ . In either case,

TABLE II  
X-RAY DIFFRACTION PATTERN OF RESIDUE  
FROM  $\text{NO}_2\text{ClO}_4$ - $\text{HClO}_4$  SOLUTION

<u>d</u>	<u><math>I/I_0</math></u>
14.98	30
9.51	5
8.08	7
7.78	3
6.78	4
6.15	10
5.45	12
5.16	30
4.74	25
4.53	40
4.25	10
4.05	12
3.88	5
3.76	7
--	--
3.49	12
3.36	2
3.27	15
3.16	100
3.09	30
2.94	40
2.34	15

TABLE III  
ANALYSIS OF  $\text{NO}_2\text{ClO}_4$ - $\text{HClO}_4$  REACTION PRODUCT

<u>Element or Group</u>	<u>Found, %</u>	<u>Calcd. for <math>\text{NO}_2\text{ClO}_4</math>, %</u>
N	9.76	9.62
$\text{ClO}_4$	68.19	68.38

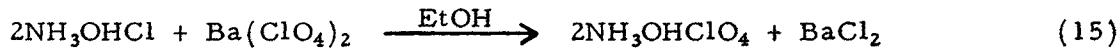
the desired perchloric acid addition compound,  $\text{NO}_2\text{ClO}_4 \cdot x\text{HClO}_4$ , was not obtained and further investigation of this system does not appear warranted.

2. Attempted Reaction of  $\text{NH}_3\text{OHClO}_4$  with  $\text{HClO}_4$

The reaction of  $\text{NH}_3\text{OHClO}_4$  with  $\text{HClO}_4$  was pursued in an attempt to prepare a new perchloric acid adduct (equation 14). The hydroxylammonium perchlorate



used was prepared by the reaction of  $\text{Ba}(\text{ClO}_4)_2$  with  $\text{NH}_3\text{OHCl}$  (equation 15)



according to the method described by Robson (Ref 6). A typical analysis of the  $\text{NH}_3\text{OHClO}_4$  obtained is given in Table IV.

TABLE IV  
ANALYSIS OF  $\text{NH}_3\text{OHClO}_4$

Type of Analysis	Found, %	Calcd., %
N	11.24	10.47
$\text{ClO}_4^-$	70.87	74.45
Neutral equiv.	136.0	133.5

Excess anhydrous perchloric acid was condensed on  $\text{NH}_3\text{OHClO}_4$  at  $-196^\circ\text{C}$ . Upon warming to room temperature some gassing was observed. After removal of the  $\text{HClO}_4$  in vacuo, however, the  $\text{NH}_3\text{OHClO}_4$  was recovered unchanged.

3. Reaction of  $\text{NH}_3\text{OHClO}_4$  with  $\text{ClO}_3\text{F}$

The reaction of  $\text{NH}_3\text{OHClO}_4$  with  $\text{ClO}_3\text{F}$  was investigated in an attempt to prepare the substituted ammonium perchlorate,  $\text{NH}_3\text{ClO}_4^+\text{ClO}_4^-$  (equation 16).



In the initial experiment,  $\text{ClO}_3\text{F}$  was added to an aqueous solution of  $\text{NH}_3\text{OHClO}_4$ . After stirring the reaction mixture for several hours the  $\text{ClO}_3\text{F}$  was recovered and the water evaporated in vacuo. The residual solid was identified by its infrared spectrum and X-ray pattern as  $\text{NH}_3\text{OHClO}_4$ .

In a second experiment,  $\text{ClO}_3\text{F}$  was added to anhydrous  $\text{NH}_3\text{OHClO}_4$ . No reaction occurred, however, even after heating the reactants for several hours at  $50^\circ\text{C}$ .

Since ammonolysis of  $\text{ClO}_3\text{F}$  in liquid ammonia is greatly accelerated by base catalysis (Ref 7), a third reaction between  $\text{ClO}_3\text{F}$  and  $\text{NH}_3\text{OHClO}_4$  was conducted in dioxane, a basic compound and an exceedingly good solvent for  $\text{ClO}_3\text{F}$ . After stirring the reaction mixture at ambient temperatures for 12 hours, a slight pressure drop was observed. Analysis of the gaseous fraction showed that it contained predominantly  $\text{ClO}_3\text{F}$ , with lesser amounts of  $\text{N}_2\text{O}$  and  $\text{CO}_2$ . Evaporation of the dioxane in vacuo yielded a pale yellow solid. The infrared spectrum of the solid, obtained as a mull, had absorptions attributable to  $\text{NH}_3\text{OHClO}_4$ . When the solid was heated at  $50^\circ\text{C}$  with pumping, however, it decomposed. The recovered  $\text{NH}_3\text{OHClO}_4$  apparently contained another component, the infrared absorptions of which were masked by those due to  $\text{NH}_3\text{OHClO}_4$ , and which accelerated the decomposition of  $\text{NH}_3\text{OHClO}_4$  when heated.

### III. EXPERIMENTAL

#### A. REACTIONS OF $N_2FAsF_6$

##### 1. With $AgClO_4$ and $NH_4SO_3F$

Samples of  $N_2FAsF_6$  dissolved in anhydrous HF were prepared in one tube of a two tube, Kel-F reactor. The two tubes were connected by a Kel-F side-arm. In the other tube, a slurry of either  $AgClO_4$  or  $NH_4SO_3F$  (each in excess) in anhydrous HF was prepared. The two solutions were mixed at room temperature, and immediate gassing was observed. The reaction was cooled to  $-80^\circ C$ , and all gases volatile at that temperature were distilled out. Identification of  $N_2O$  and  $ClO_3F$  (in the  $AgClO_4$  reaction) or  $SO_2F_2$  (in the  $NH_4SO_3F$  reaction) was accomplished by IR analysis. The approximate relative amounts of the gases were obtained from the intensities of the bands in the IR spectra. The solid residues were tested for the presence of  $N_2F^+$  by reacting it with water. No  $N_2O$  was evolved.

##### 2. With $N_2O_4$

Weighed samples of  $N_2FAsF_6$  were mixed with liquid  $N_2O_4$  in the absence of solvent. Both a 1:1 ratio of reactants and excess  $N_2O_4$  were employed. Gaseous  $NO_2$  was condensed directly onto the solid at  $-196^\circ C$  in a Kel-F reactor. The reactor was allowed to warm up to  $-80^\circ C$ , where very little reaction took place, and then slowly toward room temperature. At the melting point of  $N_2O_4$  ( $-9^\circ C$ ), a rapid evolution of gases was observed. The gaseous products were fractionated at  $-120^\circ C$  to remove unreacted  $NO_2$ . Analysis by IR spectroscopy showed the gases to be  $N_2O$  (predominant) and  $cis-N_2F_2$  (minor). Infrared analysis of the solid residue showed the presence of  $NOAsF_6$  and  $NO_2AsF_6$ .

##### 3. With $CsClF_4$ and $CsBrF_6$ in HF

Approximately equivalent solutions of  $CsClF_4$  (or  $CsBrF_6$ ) in HF and  $N_2FAsF_6$  in HF were prepared in separate legs of the two-tube Kel-F reactor. The solutions were mixed at room temperature and a slow evolution of gas was observed. The gases were distilled out of the reactor at  $-80^\circ C$  and IR analysis

showed a mixture of predominantly  $N_2O$  with small amounts of cis- $N_2F_2$ . IR spectra of mulls (Kel-F oil) of the solid residues were ill-defined, but did allow for the identification of the  $AsF_6^-$  ion. The mulling agent turned brown, however, as soon as the solid residues were added, indicating reactions between the solids and the Kel-F oil. An X-ray diffraction pattern was obtained only for the solid product from the  $CsClF_4$  reaction. (The product of the  $CsBrF_6$  reaction was very gummy, making it impossible to prepare samples for X-ray analysis.) The pattern obtained was distinct from that of  $N_2FAsF_6$  or  $CsClF_4$ . A calculated pattern was drawn up for  $CsAsF_6$  from its unit cell constants as published by Sharp (Ref 9). The most intense lines of the pattern from the  $CsClF_4$  reaction matched the calculated pattern for  $CsAsF_6$  fairly well. However, several medium intensity lines in the  $CsClF_4$  product pattern were unaccounted for, indicating the presence of an unidentified material.

#### 4. With $ClF_3$ and $BrF_5$

Excess  $ClF_3$  (or  $BrF_5$ ) was distilled directly onto solid  $N_2FAsF_6$  at  $-196^\circ C$ . On warming to room temperature vigorous boiling was observed, and IR analysis of the gaseous fraction at room temperature showed large amounts of cis- $N_2F_2$  as well as the interhalogen.

### B. REACTIONS OF cis- $N_2F_2$

#### 1. With $BiF_5$

Mixtures of solid  $BiF_5$  and excess cis- $N_2F_2$  gave no indication of reaction at room temperature even after standing several days. Heating the mixture to  $100^\circ C$  for several hours had no effect. Heating to  $160^\circ C$  (the reported melting point of  $BiF_5$ , Ref 2) caused some decomposition of the cis- $N_2F_2$ . The X-ray diffraction pattern of the solid was identical to that of the starting reactant; however, the solid did not melt at  $160^\circ C$ , or up to  $230^\circ C$ .

A slurry of  $BiF_5$  in HF was mixed with a solution of  $N_2FAsF_6$  in HF, again with no apparent signs of reaction. An X-ray pattern of the solid residue was identical to that of the original material.

#### 2. With $PF_5$

$PF_5$  and cis- $N_2F_2$  were condensed onto a  $AgCl$  window at  $-196^\circ C$ . On warming to  $-80^\circ C$  and pumping, no solid remained on the window. Condensing the material at  $-160^\circ C$  followed by pumping resulted only in condensing a film of solid  $PF_5$ . On warming the film to room temperature, no cis- $N_2F_2$  was obtained.

3. With  $\text{ClF}_3$ ,  $\text{BrF}_3$  and  $\text{BrF}_5$

These reactions were carried out in the gas phase at room temperature or above.  $\text{BrF}_3$  was converted to  $\text{BrF}_5$  by cis- $\text{N}_2\text{F}_2$  at approximately  $80^\circ\text{C}$ . There were no reactions in the cases of  $\text{ClF}_3$  and  $\text{BrF}_5$ , except some decomposition of cis- $\text{N}_2\text{F}_2$  at approximately  $150^\circ\text{C}$ .

4. With  $\text{SO}_3$ ,  $\text{SF}_4$  and  $\text{SnF}_4$

$\text{SnF}_4$  (solid) did not react with cis- $\text{N}_2\text{F}_2$  at temperatures up to  $150^\circ\text{C}$ . The mixtures were analyzed by infrared (gases) and X-ray (solid) methods.

$\text{SO}_3$  (gas) and cis- $\text{N}_2\text{F}_2$  (1:1 ratio) reacted partially at  $150^\circ\text{C}$ . Fractionation of the gases at  $-160^\circ\text{C}$  and  $-130^\circ\text{C}$ , followed by infrared analysis, showed the presence of  $\text{N}_2\text{O}$  and traces of  $\text{SO}_2\text{F}_2$ . The addition of HF resulted in almost quantitative disappearance of cis- $\text{N}_2\text{F}_2$  and  $\text{SO}_3$ . Fractionation of the gaseous products gave only  $\text{N}_2\text{O}$  and  $\text{SO}_2\text{F}_2$  in roughly equivalent amounts.

$\text{SF}_4$  and cis- $\text{N}_2\text{F}_2$  (1:1 ratio) reacted partially to give minute quantities of a white solid. Approximately 60% of the cis- $\text{N}_2\text{F}_2$  was recovered unchanged, and greater than 90% of the  $\text{SF}_4$  was recovered unchanged. Attempts were made to analyze the solid by infrared and X-ray methods, but the very small amount and the apparently hygroscopic nature of the solid rendered the results inconclusive.

5. With  $\text{NOF} \cdot 3\text{HF}$

An NMR tube was loaded with 0.218 gm (2 mmoles) of  $\text{NOF} \cdot 3\text{HF}$ . After observing the broad HF type peak at  $174 \pm 10$  ppm upfield from  $\text{CFCl}_3$ , the  $\text{NOF} \cdot 3\text{HF}$  was cooled to  $-196^\circ\text{C}$  and 2 mmoles of cis- $\text{N}_2\text{F}_2$  was added. The reaction mixture was allowed to stand at room temperature for several hours. The HF type peak was now found to be  $187 \pm 6$  ppm upfield from  $\text{CFCl}_3$ . The tube was then evacuated and a white solid was obtained. The X-ray diffraction pattern of this solid is given in Table I (Discussion Section).

C. PREPARATION OF trans- $\text{N}_2\text{F}_2$

1. Reaction of  $\text{N}_2\text{F}_4$  with  $\text{AsF}_5$

$\text{N}_2\text{F}_4$  and  $\text{AsF}_5$  (1:2 mole ratio) at a total pressure of 2-3 atmospheres were mixed in a high-pressure glass reactor (Fisher-Porter tube). The formation of

a white solid occurred slowly, accompanied by a gradual decrease in the total pressure. On standing overnight at room temperature a 55% decrease in total pressure occurred. The unreacted gases were fractionated, measured quantitatively, and analyzed. The gaseous fraction consisted of unreacted  $N_2F_4$  and  $AsF_5$ , along with small amounts of impurities originally present in the original reactants ( $SiF_4$ ,  $BF_3$ ). To date, the quantitative measurements have not been consistent or reproducible.

Thermal decomposition of the solid adduct occurred at room temperature to give trans- $N_2F_2$  and  $N_2F_4$  as identified by infrared analysis. An X-ray pattern of the solid residue showed it to be isomorphous with  $NOAsF_5$ ,  $O_2AsF_6$ .

## 2. Formation of trans- $N_2F_2$

Samples of the adduct were caused to react with NO by condensing an excess of NO onto the solid at  $-196^{\circ}C$ , warming the reactor to room temperature and allowing it to remain at that temperature for about one hour. Fractionation at  $-160^{\circ}C$  and  $-196^{\circ}C$  afforded trans- $N_2F_2$  (approximately 50% of the N-F material),  $N_2F_4$ , unreacted NO, and occasionally varying amounts of  $NF_3$ . Separation and purification of the trans- $N_2F_2$  was accomplished by vapor phase chromatography using Linde 13X molecular sieves.

## D. ATTEMPTS TO PREPARE NEW PERCHLORATES

### 1. Attempted Reaction of $NO_2ClO_4$ and $HClO_4$

Anhydrous  $HClO_4$  was prepared by dehydrating 70%  $HClO_4$  with the requisite amount of fuming  $H_2SO_4$ . The  $HClO_4$  generated was collected at  $-78^{\circ}C$  and then transferred to a trap containing the  $NO_2ClO_4$  cooled to  $-196^{\circ}C$ . For example, approximately 1.5 cc of anhydrous  $HClO_4$  was condensed on 0.34 gm of  $NO_2ClO_4$  at  $-196^{\circ}C$ . The reaction mixture was allowed to warm to room temperature with stirring. Subsequently, the excess  $HClO_4$  was removed in vacuo. The X-ray powder pattern of the residual white solid is given in Table II and the chemical analysis in Table III. (Tables are in Discussion Section.)

### 2. Attempted Reaction of $NH_3OHClO_4$ and $HClO_4$

To 0.267 gm (2mmoles) of  $NH_3OHClO_4$  at  $-196^{\circ}C$  was added approximately 2 cc of anhydrous  $HClO_4$ . The reaction mixture was allowed to warm to room temperature. After stirring for 15 minutes at ambient temperatures the  $HClO_4$  was slowly removed in vacuo. The  $NH_3OHClO_4$  was found to be unchanged on the basis of X-ray analysis.

3. Attempted Reaction of  $\text{NH}_3\text{OHCLO}_4$  with  $\text{ClO}_3\text{F}$

(a) Aqueous Solution - To a solution of 0.4846 gm (3.63 mmoles) of  $\text{NH}_3\text{OHCLO}_4$  in 5 ml of water at  $-196^\circ\text{C}$  was added 4.5 mmoles of  $\text{ClO}_3\text{F}$ . The reaction mixture was then allowed to warm to room temperature. No change in pressure was observed even after stirring the mixture for several hours. The  $\text{ClO}_3\text{F}$  was recovered, and the unreacted  $\text{NH}_3\text{OHCLO}_4$  was isolated by pumping on the aqueous solution at  $50^\circ\text{C}$ .

(b) No Solvent - To 0.467 gm (3.50 mmoles) of  $\text{NH}_3\text{OHCLO}_4$  at  $-196^\circ\text{C}$  was added 4.0 mmoles of  $\text{ClO}_3\text{F}$ . The reaction mixture was allowed to warm to room temperature and then heated at  $50^\circ\text{C}$  for several hours with stirring. Both the  $\text{ClO}_3\text{F}$  and  $\text{NH}_3\text{OHCLO}_4$  were recovered unchanged.

(c) In Dioxane - To a solution of 0.5342 gm (4.0 mmoles) of  $\text{NH}_3\text{OHCLO}_4$  in 20 ml of dioxane cooled to  $-196^\circ\text{C}$  was added 4 mmoles of  $\text{ClO}_3\text{F}$ . The reaction mixture was stirred at ambient temperatures for 12 hours. A slight pressure drop was observed. The gaseous fraction contained predominantly  $\text{ClO}_3\text{F}$  with lesser amounts of  $\text{N}_2\text{O}$  and  $\text{CO}_2$ . Evaporation of the solvent in vacuo yielded a pale yellow solid exhibiting an infrared spectrum with absorptions attributable to  $\text{NH}_3\text{OHCLO}_4$ . An attempt to dry the solid further by pumping on it at  $50^\circ\text{C}$  resulted in decomposition of the entire mass.

#### IV. FUTURE WORK

Future work will be concentrated in four areas, namely: (1) continuation of the efforts to prepare  $N_2FClO_4$  and  $N_2FClF_4$ ; (2) characterization of the  $N_2F_4 \cdot xAsF_5$  adduct; (3) hot tube reactions of cis- $N_2F_2$  with suitable O-N-F radical sources, and (4) identification of the solid residue obtained by distilling  $NOF \cdot 3HF$ .

In the attempts to prepare  $N_2FClO_4$  and  $N_2FClF_4$ , particular attention will be directed to finding and utilizing solvents other than HF (IF<sub>5</sub> appears to be the most promising solvent medium investigated thus far). We also intend to investigate the possibility of forming these compounds by solid state reactions, rather than in solution.

The composition of the  $N_2F_4 \cdot xAsF_5$  adduct, it is hoped, will be determined by careful preparative measurements. Low temperature infrared studies should yield considerable information concerning the structure of the adduct.

A series of hot tube reactions of cis- and trans- $N_2F_2$  with NO, NO- $N_2F_4$ , and other N-F mixtures will be carried out. Particular emphasis will be directed toward improving the yields of products by carefully controlling the reaction conditions.

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